

# **PHASE CHARACTERISATION AND BENEFICIATION STUDIES ON LOW GRADE WOLFRAMITE ORE AND SYNTHETIC SAMPLES**

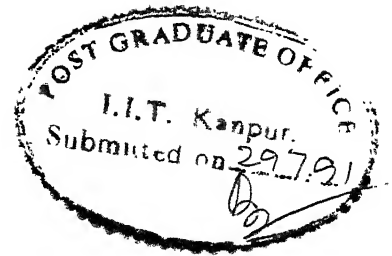
*A Thesis Submitted  
in Partial Fulfilment of the Requirements  
for the Degree of  
MASTER OF TECHNOLOGY*

*by*

Miss. MANJUSHA V. SAKHARKAR

**to the**

**DEPARTMENT OF METALLURGICAL ENGINEERING  
INDIAN INSTITUTE OF TECHNOLOGY KANPUR  
JULY, 1991**



## CERTIFICATE

It is certified that the work contained in the thesis entitled "Phase characterisation and beneficiation studies on low grade wolframite ore and synthetic samples" has been carried out by Miss Manjusha V. Sakharkar under my supervision and that this work has not been submitted elsewhere for a degree.

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MANJUSHA V. SAKHARKAR

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Indian wolframite is a low-manganese phase highly dispersed in quartz matrix. Comminution and preliminary magnetic separation should be followed by hydrometallurgical dissolution with alkali, preferably aided by some complexing reagent for speedy removal of ferrous ions into the solution.

## CHAPTER 1

### INTRODUCTION

1.1 Wolframite is a tungsten bearing mineral in the form of  $(\text{Fe,Mn})\text{WO}_4$ . The unique high temperature properties of tungsten and its alloys are responsible for the increased demand of this metal, particularly in the form of carbide and pure metal. It is also an important strategic material for defence, nuclear and space research applications. India is importing large quantities of tungsten concentrate to meet domestic demand. The production of concentrate in our country is very meagre and restricted to high grade tungsten deposits of limited extent. As such there is an urgent need for the beneficiation of the vast low grade ore deposits available in the country [1].

Processing new kinds of ore and low grade ores will require new and superior technology and the need is increasing day by day. As the world's supply of mineral raw materials diminishes, lower grade ores will have to be sought as new sources of metal and minerals [2]. Advanced mining and size reduction techniques will be needed to deal with the problem of finding ways to reduce unnecessary fines. To meet increasing energy, environmental and economic constraints, ever-expanding research in fine particles characterisation and processing will grow.

#### 1.2 RAW MATERIAL AVAILABLE

One of the potential reserves of the metal in the form of mineral wolframite are the phyllite deposits of Degana,

Rajasthan, with an estimated ore reserves of 2.72 millions tonnes containing about 1000 tonnes of metal [1]. At Degana, the low grade tungsten occurs in three types of deposits, viz, vein, stock work (phyllite formation) and alluvial. Some work has been carried out on vein and alluvial deposits by Indian Bureau of Mines [1] and very little work has been reported on phyllite deposits. In the light of strategic importance of tungsten, an attempt has been made to assess the amenability of the phyllite ore to beneficiation by gravity and magnetic separations after detailed mineralogical studies.

### 1.3 MINEROLOGY AND ORE ANALYSIS

From the literature available, it is seen that the mineralogy of this ore is very complex in nature [1]. Mineralogical analysis shows that the ore consists mainly of quartz, mica, iron oxides as chief gangue minerals. The other gangue minerals identified are pyrite, graphite, topaz, fluorite.

Quantitative analysis shows that it contains 0.032 to 0.063%  $WO_3$ , 6.66%  $Fe_2O_3$ , 14.3%  $Al_2O_3$  and 67.4%  $SiO_2$ . The polished section of sample, seen under microscope shows that most of wolframite is associated with quartz [1]. Most of the minerals occurring as fine grained have graphite and iron hydroxide coating. Wolframite is seen to occur as fine grained (0.05 to 0.1 mm), subhedral to euhedral fragments, mostly associated with quartz. Some grains are also associated with pyrite [1]. Hematite is found to occur as fine to medium size irregular grains, mostly along the grain boundaries of quartz. Fine to coarse (0.01 to 0.5



mm) grains of pyrite are found in the sample and most of them are interlocked with quartz. Graphite is found as clusters of thin flakes and also sheaflike aggregates along the quartz grain boundaries.

The approximate mineralogical composition of a representative sample is shown in Table 1-1.

TABLE 1-1 [1]

Mineral	% by Volume	Chemical Constituent	%
Quartz	56-70	$\text{SiO}_2$	65.40
Mica	7-10	$\text{Al}_2\text{O}_3$	14.30
Iron-oxides	5-7	$\text{Fe}_2\text{O}_3$	6.66
Graphite	1-2	CaO	7.30
Pyrite	3-4	MgO	3.26
Topaz	2-3	$\text{TiO}_2$	0.28
Ilmenite	1-2	Pyrite sulphur	1.28
Fluorite	1-2	Fixed carbon	0.66
Tourmaline	< 1	$\text{Na}_2\text{O}$	0.48
Chalcopyrite	< 1	$\text{WO}_3$	0.032 to 0.063
Sphalerite	< 1		
Arsenopyrite	< 1		
Wolframite	< 1		

Spectrophotometric analysis [4] was done to estimate tungsten, and analysis of other elements was carried out according to procedures described by Vogel [5].

#### 1.4 OBJECTIVES OF THE PRESENT WORK

- a) One of the objectives of this work has been to characterise this raw material. For that liberation studies were carried out using a high resolution optical microscope to derive the idea about physical association of minerals in the sample. Phase characterisation studies were carried out to find the minerals present, both valuable and gangue. The techniques adopted in this study are X-ray diffraction, scanning electron microscope. Liberation and phase characterisation studies also helped in selecting the beneficiation techniques. The current industrial procedure for the processing of tungsten concentrated into metal powder is tabulated in Appendix.
- b) Another goal has been to study selectivity in the leaching of wolframite ore. Leaching of wolframite can be done by NaOH or  $\text{Na}_2\text{CO}_3$ . But we were basically interested in understanding the mechanism of NaOH interaction on wolframite. We were also interested in the kinetics of the leaching process. The crystal structure of both wolframite and scheelite is given in Appendix.

We have tried to achieve this goal by carrying out leaching on specially synthesized and characterised series of wolframite and analysing the resultant solutions as well as the solid residue using SEM and X-ray diffraction methods.

## CHAPTER 2

### STUDIES ON RAW MATERIALS

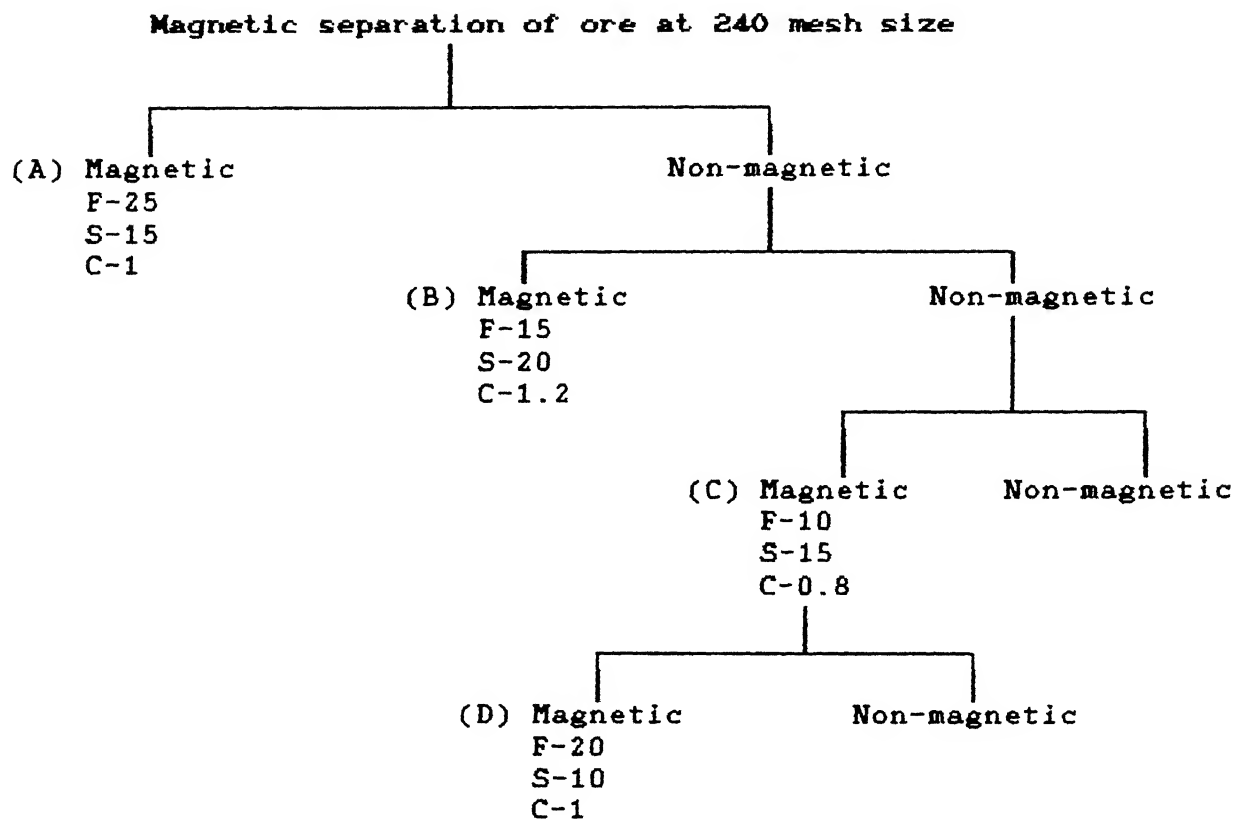
The wolframite ore sample was supplied by the Indian Bureau of Mines, Rajasthan. We have analysed that sample by various techniques like X-ray diffraction, electron microscopy and chemical analysis after preliminary beneficiation.

#### 2.1 PRELIMINARY BENEFICIATION STUDIES

The ore was first crushed and ground and then sieved at 240 mesh size. It was considered advisable to wash the sample before treatment in order to remove the dust adhering to the grains. Particles were then subjected to magnetic separation in Frantz Isodynamic Magnetic Separator.

The separator consists essentially of an electromagnet having two long pole pieces shaped to a special contour with long narrow air gap between them. Material to be separated are fed into the space between the pole pieces and travel parallel to their length. The more highly magnetic particles are urged towards the narrow side of the air gap. The grains are intercepted by a dividing edge which directs the two fractions to separate containers. We got different fractions at different angles and currents.

Initially we tried to get the fractions with varying current and angle. But we failed to get any good result. Then we changed the conditions and we got four fractions at different angles and currents.



where F → Forward angle in degrees

S → Side angle in degrees

C → Current in amperes

The schematic table is as follows. These four samples were -

TABLE 2-1

Magnetic Sample	Side Angle (degree)	Forward Angle (degree)	Current (ampere)
A	15	25	1
B	20	15	1.2
C	15	10	0.8
D	10	20	1

After carrying out X-ray diffraction of these samples, sample D showed more peaks of wolframite as compared to A, B, C.

## 2.2 X-RAY DIFFRACTION STUDY

X-ray diffraction studies were carried out on fractions obtained through magnetic separation. The small amount of powder sample (minus 240 mesh) was taken in a perspex specimen holder and mounted on the specimen stage of diffractometer. Copper  $K\alpha$  radiation with Nickel filter was used and the intensity vs  $2\theta$  plots were recorded on a chart paper.

## PREAMBLE FOR X-RAY DIFFRACTION WORK

The interplanar spacing 'd' were calculated from Bragg's law  $\lambda = 2d \sin\theta$ , where  $\lambda$  = wavelength of characteristics radiation used ( $\lambda = 1.542 \text{ \AA}$ ) and  $\theta$  is the angle at which reflection takes place which was obtained from the diffraction peaks. The relative intensities were also calculated. Then attempts were made to identify the minerals by comparing the first three strongest 'd'

values with those of various possible mineral. But due to presence of large number of phases it was not possible to do so. So corresponding to each 'd' value, a list of probable compounds whose one of the 'd' values lies within range  $\pm 0.015 \text{ \AA}^0$  was made. Hence such a list against each 'd' value take into account all probable phases that might be present in the sample. Finally the number of times a phase had appeared was also listed. The higher the number of appearances, more was the possibility of existence of that phase. The presence of such phases were also independently verified by electron diffraction.

From all the diffraction patterns we can conclude that the chief gangue minerals associated with wolframite are hematite, graphite, mica, scheelite, arsenopyrite, ilmenite and chalcopyrite. Sample D contains relatively greater proportion of wolframite.

The X-ray diffraction tables are as follows :

#### X-ray Diffraction Pattern of Sample A

TABLE 2-2 [101]

Sl.No.	$2\theta$	I	d	Mineral	
1.	21.3	30.5	4.189		
2.	26.8	60.0	3.340	Graphite	3.3480
				Hematite	3.34
3.	24.4	23.0	3.663	Wolframite*	3.648
				Arsenopyrite	3.658
4.	25.8	24.0	3.467		
5.	27.6	28.5	3.245	Hematite	3.24

contd...

Table 2-2 contd...

Sl.No.	2θ	I	d	Mineral	
6.	28.1	44.0	3.189		
7.	29.5	22.0	3.04	Chalcopyrite	3.038
8.	30.5	19.5	2.943	Wolframite	2.953
9.	30.8	19.0	2.915		
10.	36.9	19.0	2.446	Arsenopyrite	2.440
				Hematite	2.458
11.	40.6	15.0	2.231	Hematite	2.243
				Ilmenite	2.237
12.	42.7	17.0	2.126	Graphite	2.127
13.	43.1	14.0	2.107	Ilmenite	2.103
14.	45.9	13.0	1.985	Scheelite	1.995
				Hematite	1.983
15.	46.1	13.0	1.977	Hematite	1.973
				Muscovite	1.966
16.	50.3	23.0	1.82	Arsenopyrite	1.824
				Wolframite	1.833
				Ilmenite	1.830
17.	50.9	16.5	1.801	Hematite	1.807
				Arsenopyrite	1.814
18.	60.2	19.0	1.543	Arsenopyrite	1.543
				Graphite	1.539
19.	67.9	14.0	1.386	Scheelite	1.385
				Hematite	1.383
20.	55.1	12.0	1.673	Scheelite	1.68
				Hematite	1.666
21.	60.0	15.0	1.548	Scheelite	1.553
				Sphalerite	1.561
22.	68.5	25.0	1.375	Wolframite	1.375
				Ilmenite	1.3757
				Hematite	1.383

contd...

Table 2-2 contd...

Sl.No.	2 $\theta$	I	d	Mineral	
23.	80.2	10.0	1.201	Ilmenite	1.204
				Chalcopyrite	1.205
				Sphalerite	1.209
24.	81.7	11.5	1.183	Scheelite	1.190
				Ilmenite	1.187
25.	90.9	10.0	1.086	Wolframite	1.086
				Scheelite	1.087
26.	91.2	9.5	1.0836	Scheelite	1.083
				Ilmenite	1.088
27.	96.5	9.0	1.0377	Scheelite	1.035

\* Standard values compared to wolframite mineral and not the synthetic samples.

Sample A TABLE 2-3

Mineral	Number of time it appeared
Hematite	10
Scheelite	8
Ilmenite	7
Wolframite	5
Arsenopyrite	5
Graphite	3
Chalcopyrite	2
Sphalerite	2



Sample B TABLE 2-4

Sl.No.	2θ	I	d	Mineral	
1.	21.2	24.0	4.20		
2.	26.8	58.0	3.34	Graphite	3.348
				Hematite	3.34
3.	27.1	57.0	3.304		
4.	28.1	28.0	3.189	Sodium Tungstate	3.173
5.	36.9	13.0	2.446	Arsenopyrite	2.440
				Hematite	2.458
6.	41.9	11.5	2.165		
7.	39.6	14.0	2.285	Hematite	2.295
8.	42.7	15.0	2.126	Graphite	2.1270
9.	45.8	14.0	1.9897	Hematite	1.997
				Muscovite	1.999
				Scheelite	1.995
10.	50.4	32.0	1.818	Arsenopyrite	1.814
				Hematite	1.807
11.	51.1	16.0	1.795	Graphite	1.795
				Arsenopyrite	1.787
12.	55.2	12.0	1.671	Graphite	1.674
				Hematite	1.666
13.	60.3	18.0	1.541	Arsenopyrite	1.543
				Graphite	1.5398
				Hematite	1.537
				Muscovite	1.551
14.	67.9	15.0	1.386	Scheelite	1.385
				Hematite	1.383
				Arsenopyrite	1.390
15.	68.4	20.5	1.377	Wolframite	1.375
				Ilmenite	1.3757
				Scheelite	1.385
16.	75.9	13.0	1.258	Scheelite	1.248
				Fluorite	1.253

contd...

Table 2-4 contd...

Sl.No.	2 $\theta$	I	d	Mineral	
17.	76.1	12.0	1.256	Scheelite	1.248
				Fluorite	1.253
18.	80.2	9.0	1.2019	Wolframite	1.1940
				Chalcopyrite	1.2052
				Ilmenite	1.2040

Sample B TABLE 2-5

Mineral	Number of time it appeared
Hematite	8
Scheelite	5
Arsenopyrite	5
Graphite	5
Wolframite	2
Ilmenite	2

Sample C TABLE 2-6

Sl.No.	2 $\theta$	I	d	Mineral	
1.	9.2	65.0	9.653		
2.	21.0	30.0	4.248		
3.	26.9	90.0	3.328	Muscovite	3.331
4.	28.0	44.0	3.20		
5.	30.7	17.0	2.924		
6.	36.8	16.0	2.452	Hematite	2.458
				Arsenopyrite	2.440

contd...

Table 2-6 contd...

Sl.No.	2 $\theta$	I	d	Mineral	
7.	39.7	14.0	2.280	Hematite	2.295
8.	42.7	17.0	2.126	Graphite	2.1270
9.	45.9	16.5	1.985	Hematite	1.983
				Scheelite	1.995
10.	50.3	20.5	1.82	Wolframite	1.833
				Arsenopyrite	1.824
11.	55.4	17.0	1.665	Hematite	1.666
12.	55.5	17.2	1.662	Hematite	1.666
13.	60.2	17.0	1.543	Arsenopyrite	1.543
				Graphite	1.5398
				Scheelite	1.553
14.	68.4	22.0	1.377	Wolframite	1.375
				Ilmenite	1.3757
				Fluorite	1.365
15.	67.9	12.0	1.386	Scheelite	1.385
				Hematite	1.383
				Ilmenite	1.375
				Arsenopyrite	1.390

Sample C      TABLE 2-7

Mineral	Number of time it appeared
Hematite	5
Arsenopyrite	4
Wolframite	3
Ilmenite	2
Graphite	2
Scheelite	3

Sample D TABLE 2-8

Sl.No.	2 $\theta$	I	d	Mineral	
1.	21.2	24.0	4.208	Sodium Tungstate 4.210	
2.	26.9	76.5	3.328	Muscovite	3.331
3.	27.4	50.0	3.268		
4.	27.9	45.5	3.211		
5.	28.1	44.5	3.189		
6.	30.6	19.0	2.933		
7.	39.7	15.0	2.280	Hematite	2.295
8.	42.8	16.0	2.121	Graphite	2.1270
9.	36.8	21.5	2.45	Hematite	2.458
				Arsenopyrite	2.440
10.	43.2	25.0	2.10	Ilmenite	2.1032
				Arsenopyrite	2.096
11.	43.9	18.0	2.071	Wolframite	2.061
12.	45.7	20.0	1.993	Muscovite	1.999
				Wolframite	2.006
				Hematite	1.997
13.	46.0	19.0	1.981	Hematite	1.983
14.	50.5	19.5	1.814	Hematite	1.807
				Arsenopyrite	1.814
15.	51.3	15.0	1.788	Arsenopyrite	1.787
16.	55.3	17.0	1.668	Hematite	1.666
				Ilmenite	1.653
17.	60.3	18.0	1.541	Arsenopyrite	1.543
				Graphite	1.5398
				Hematite	1.537
18.	68.0	17.0	1.384	Wolframite	1.391
				Hematite	1.383
				Scheelite	1.385
				Arsenopyrite	1.390

contd...

Table 2-8 contd...

Sl.No.	2 $\theta$	I	d	Mineral	
19.	68.5	30.0	1.375	Wolframite	1.375
				Scheelite	1.385
				Ilmenite	1.3757
20.	81.6	10.0	1.184	Wolframite	1.194
				Scheelite	1.190
				Ilmenite	1.1871
21.	91.3	10.0	1.082	Wolframite	1.086
				Scheelite	1.083
				Ilmenite	1.088

Sample D      TABLE 2-9

Mineral	Number of time it appeared
Hematite	9
Wolframite	6
Arsenopyrite	6
Ilmenite	5
Scheelite	5
Graphite	2

### 2.3 CHEMICAL ANALYSIS OF MAGNETICALLY SEPARATED FRACTIONS

The four magnetically separated fractions were chemically analysed. Since it was a low grade tungsten bearing mineral ore, the tungsten content was analysed by a spectrophotometer [4]. Also from SEM, the result show very less amount of manganese. So Mn was also analysed by the spectrophotometer.

### A) METHOD FOR DETERMINATION OF $\text{SiO}_2$ AND TOTAL Fe

i) 0.5 gm sample was dissolved in a mixture of hydrochloric, sulphuric and nitric acid (10 ml each) and baked for 3 hrs. to dryness. After cooling, the material was again boiled with water and hydrochloric acid. The solution was filtered and washed with hot water 4 to 5 times. The residue was ignited in platinum crucible and then weighed. After that few drops of  $\text{H}_2\text{SO}_4$  and 5 ml hydrofluoric acid were added to the residue. The residue was ignited and weighed. The difference gave  $\text{SiO}_2\%$ .

ii) For total Fe

After separation of  $\text{SiO}_2$ , the filtrate was taken and boiled. Stannous chloride was added to the filtrate till it became colourless and cooled. To the filtrate, 10 ml  $\text{HgCl}_2$  and acid mixture ( $\text{H}_2\text{SO}_4 + \text{H}_3\text{PO}_4$ ) were added. It was then titrated with potassium dichromate ( $\text{K}_2\text{Cr}_2\text{O}_7$  0.1N) using Diphenyl amine as indicator. At the end point, the filtrate turned to violet colour.

### B) METHOD FOR DETERMINATION OF Mn BY SPECTROPHOTOMETER

0.1 gm sample was dissolved in mixture of  $\text{HCl} + \text{H}_2\text{SO}_4 + \text{HNO}_3$  (10 ml each) and baked for 3 hrs. After fuming off, water and little amount of  $\text{HNO}_3$  were added and the whole mixture was boiled. After filtration, potassium periodate was added to filtrate while boiling. The colour developed was analysed in

a spectrophotometer at 525 nm wavelength. From the standard calibration curve, the amount of manganese was estimated.

C) METHOD FOR DETERMINATION OF TUNGSTEN BY SPECTROPHOTOMETER [4]

0.1 to 0.2 gm finely pulverised sample was fused with 0.5 to 1 gm of potassium pyrosulphate to red hot melt and kept in this condition for at least 10 minutes. Then the material was removed from flame and allowed to cool. The cake was dissolved by boiling with 75-100 ml of 0.5 M tartaric acid. The resultant solution was filtered through no. 40 Whatman paper, and the residue washed with hot water containing a pinch of tartaric acid. To the filtrate, 10 ml concentrated  $H_2SO_4$ , 20 ml of 12N HCl and 5 ml 2N stannous chloride were added and the beaker was placed in a boiling water bath for half an hour. To that, 10 ml water was added and finally cooled to 10-15°C. 10 ml of 20% potassium thiocyanate solution was added. The solution was taken in 100 ml flask and volume made up with distilled water. After colour formation, the transmittance was measured on the spectrophotometer at wavelength 400 nm.

The  $WO_3\%$  was calculated from calibration curve using standard tungsten solutions.

TABLE 2-10  
ANALYSIS OF THE MAGNETICALLY SEPARATED FRACTIONS

Sample	SiO <sub>2</sub> %	Fe%	Mn%	WO <sub>3</sub> %
A	25.18	1.12	0	0.070
B	39.14	4.96	0.16	0.033
C	59.58	7.68	0.19	0.0562
D	55.70	8.44	0.01	0.06

From the above result we conclude that the ore contains very low grade tungsten and manganese. Fractions A and D are richer in tungsten.

#### 2.4 SEM ANALYSIS OF RAW MATERIAL

The magnetically separated fractions were studied under Scanning Electron Microscope (SEM), in the secondary electron mode, under an operating voltage of 20 KV. The quantitative analysis seeks to establish not only the identities of element present but also their concentrations. This analysis was done with the help of energy dispersive system EDAX. The EDAX system detect the location of spectral peaks, compare them with tabulated energy values, check for inconsistencies, then print out the list of elements present.

The calculated elemental concentrations are then based on the concentrations of the theoretical standards and the matrix corrected K-ratios. The K ratio is the ratio of peak intensity of unknown to the peak intensity of the standard. Excellent quantitative results can also be obtained by establishing a



calibration curve from the analysis of several samples of known composition. It is then a simple procedure to derive elemental concentration directly from the X-ray intensity in the range of the curve. The only rigid requirements are that of acquisition conditions be identical for calibration of standard and sample and that the composition of the sample be similar to that of standard.

In SEM, conventionally beryllium-window detectors cannot detect oxygen X-rays which are absorbed before reaching the detector. The beryllium window of the traditional detector absorbs most of the radiation from the elements lighter than sodium. However, geologists for example, must often analyse stable oxides common in mineralogical specimens. This is commonly done by stoichiometry.

The assumption is made that all oxygen present in sample is in the form of oxides having known formulas. At each iterative step in the normal ZAF analysis, oxygen is included as an undetected constituent present at the level indicated by the intensities of the signals from the other components of the oxides e.g. if  $\text{Fe}_2\text{O}_3$  is assumed to be present, then for every atom of iron indicated by its X-ray intensity,  $1\frac{1}{2}$  atoms of oxygen are assumed to be absorbing fluorescing X-rays within the sample. The ZAF corrections then take account of assumed amount of oxygen. In ZAF correction, Z indicates atomic number, A indicates absorbance and F indicates fluorescence. For each element the analysis chart shows standard deviation of the actual value.

For SEM sample was prepared by the following method :

The graphite solution or silver iodide paste was applied on a small brass stub. The powdered sample was then spread over it. After drying, silver coating was done to make it conducting. The stub was then placed on a holder and inserted in the microscope.

From the analysis chart we calculated Fe/Mn and Fe/W ratios in atomic proportion to check it with actual theoretical ratios. Some of the values are nearly close to the theoretical values. The elemental analysis for sample A, B, C and D are as follows.

Elemental Analysis by SEM

SAMPLE A

TABLE 2-11

Element	Weight %	Relative Atomic Proportion [ $\frac{\text{wt \%}}{\text{At.wt.}}$ ]	Weight Proportion		Atomic Proportion	
			Fe/Mn	Fe/W	Fe/Mn	Fe/W
Al	4.08	0.051				
Si	16.83	0.599				
S	0.03	$9.3 \times 10^{-4}$				
Ca	0.85	0.021				
Ti	0.06	$1.2 \times 10^{-3}$				
Mn	0.00	0.00				
Fe	2.64	0.0472	$\infty$	0.064	$\infty$	0.251
W	40.86	0.188				
O	34.65					

SAMPLE BTABLE 2-12

Element	Weight %	Relative Atomic Proportion [ $\frac{\text{wt \%}}{\text{At.wt.}}$ ]	Weight Proportion		Atomic Proportion	
			Fe/Mn	Fe/W	Fe/Mn	Fe/W
Al	5.57	0.206				
Si	11.58	0.412				
Ca	1.85	0.046				
Ti	1.24	0.258				
Mn	1.71	0.031				
Fe	15.42	0.276				
Ba	3.03	0.022	9.017	0.566	8.90	1.877
W	27.20	0.147				
O	32.16					

SAMPLE CTABLE 2-13

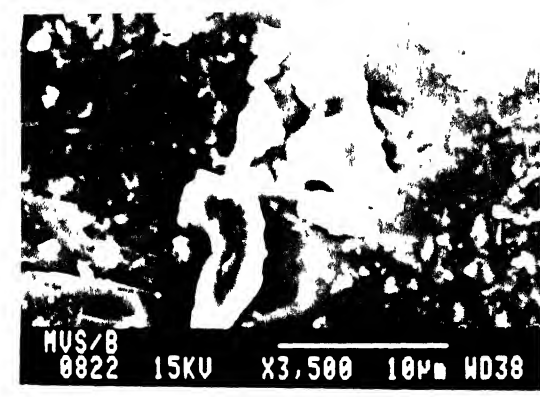
Element	Weight %	Relative Atomic Proportion [ $\frac{\text{wt \%}}{\text{At.wt.}}$ ]	Weight Proportion		Atomic Proportion	
			Fe/Mn	Fe/W	Fe/Mn	Fe/W
Mg	0.49	0.020				
Al	5.45	0.202				
Si	11.56	0.411				
S	1.17	0.036				
Ca	1.87	0.046				
Ti	1.41	0.0294				
Fe	16.72	0.299	$\infty$	0.613	$\infty$	2.02
Mn	0.00	0.00				
W	27.27	0.148				
O	33.76					

SAMPLE DTABLE 2-14

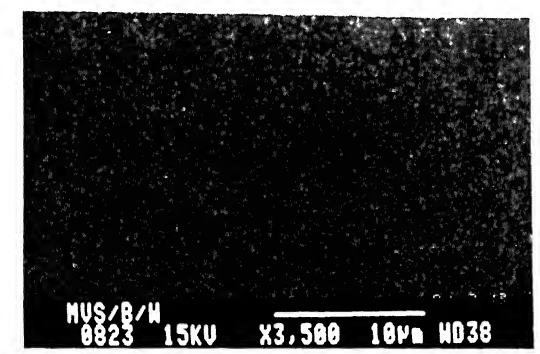
Element	Weight %	Relative Atomic Proportion [ $\frac{\text{wt \%}}{\text{At.wt.}}$ ]	Weight Proportion		Atomic Proportion	
			Fe/Mn	Fe/W	Fe/Mn	Fe/W
Si	19.10	0.680				
Ca	0.05	$1.2 \times 10^{-3}$				
Ti	0.06	$1.2 \times 10^{-3}$				
Mn	0.04	$7.28 \times 10^{-4}$				
Fe	0.15	$2.68 \times 10^{-3}$	3.75	$3.22 \times 10^{-3}$	3.68	0.010
W	46.58	0.253				
O	34.03					

From X-ray and elemental analysis, it was seen that the ore contains some amount of scheelite. X-ray analysis shows greater proportion of scheelite in the samples A and D. Ilmenite was also present in A and D in large proportion. The ore contains large amount of iron-oxides. Iron was present in the form of pyrite, hematite, arsenopyrite, ilmenite. So the amount of iron was more in A, B and D.

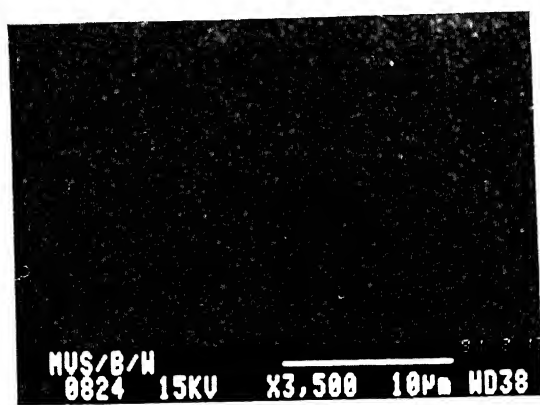
Sample A and D were rich in wolframite. The X-ray mapping of these four sample shows the distribution of Si, Al, Fe, and W in a particle. We have also tried for line profile method in which the distribution of element was shown by peaks of various intensities. But this method was not suitable for our sample as there was uniform distribution of Si and W. The photomicrographs of X-ray mapping and line profile are as follows.



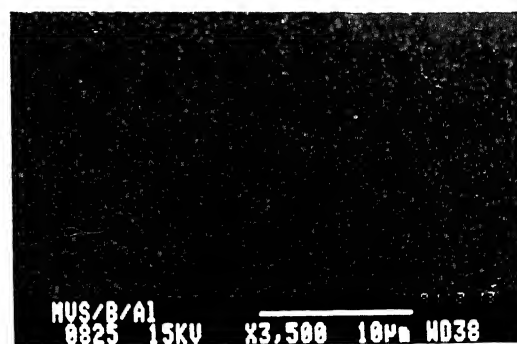
(a)



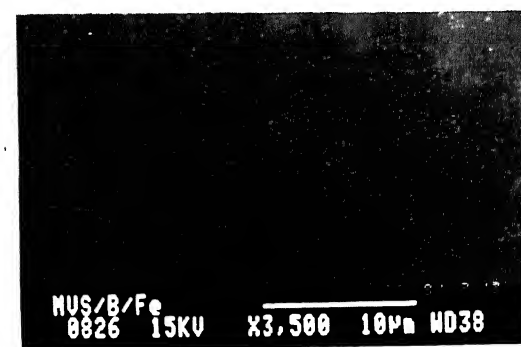
(b)



(c)

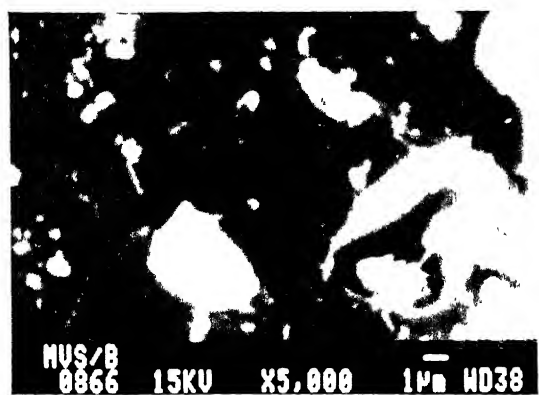


(d)

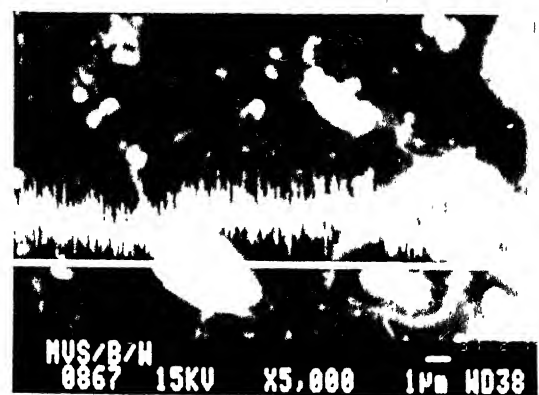


(e)

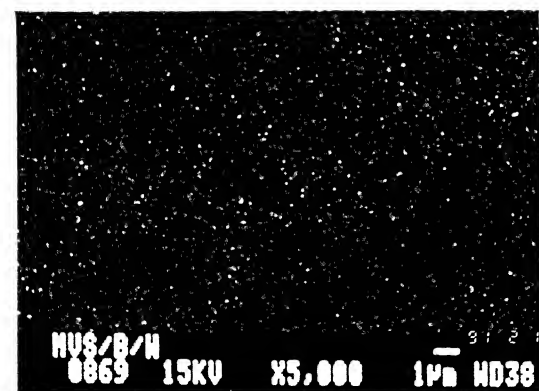
Fig. 2-1.2 : X-ray mapping of sample B with a) micrograph, b) Si, c) W, d) Al, e) Fe distribution.



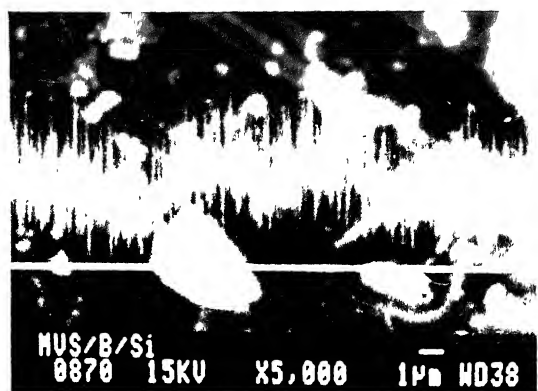
(a)



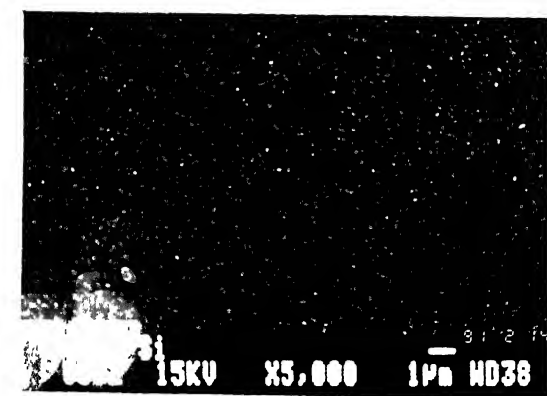
(b)



(c)

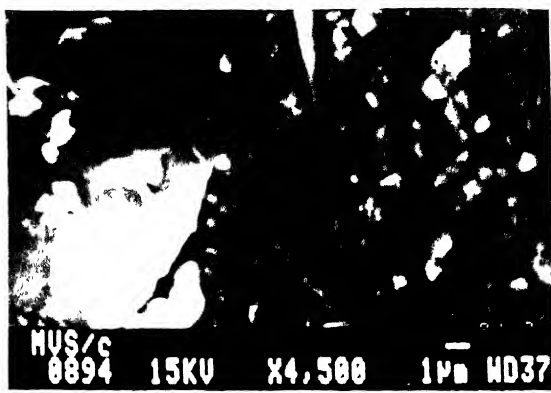


(d)

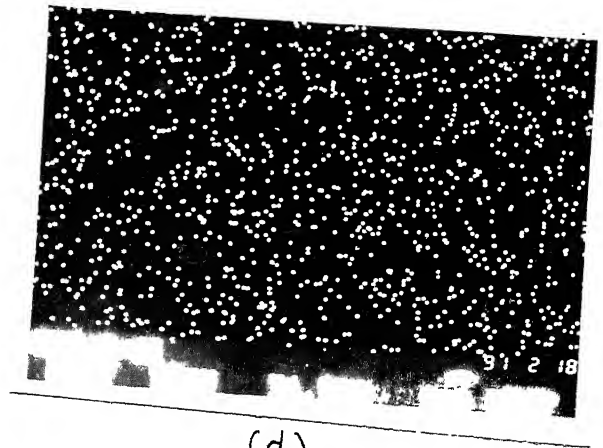


(e)

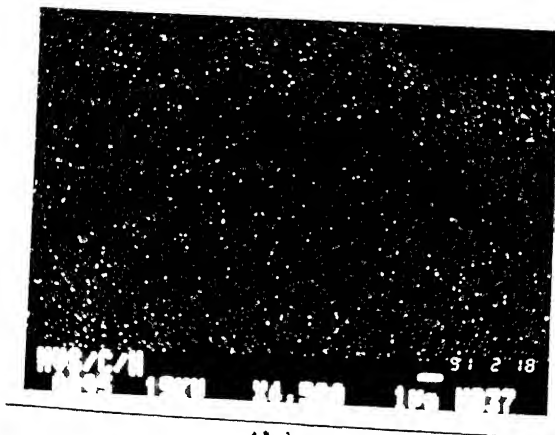
Fig. 2-1.3 : Line profile and X-ray mapping of sample B with  
 a) micrograph, b) line profile of W, c) W distribution.  
 d) line profile of Si, e) Si distribution.



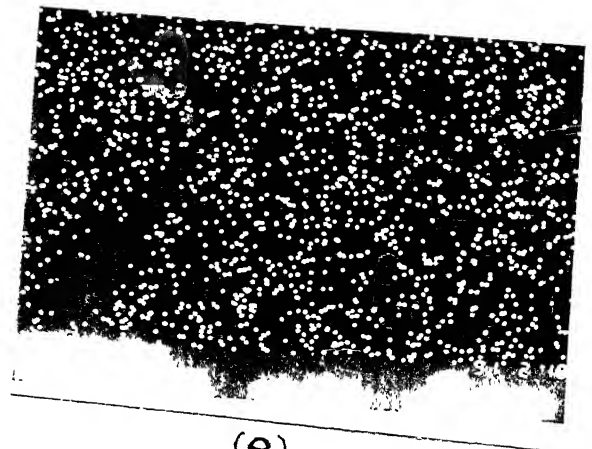
(a)



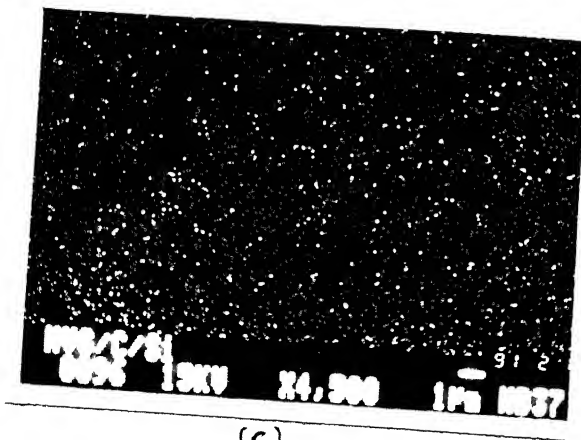
(d)



(b)

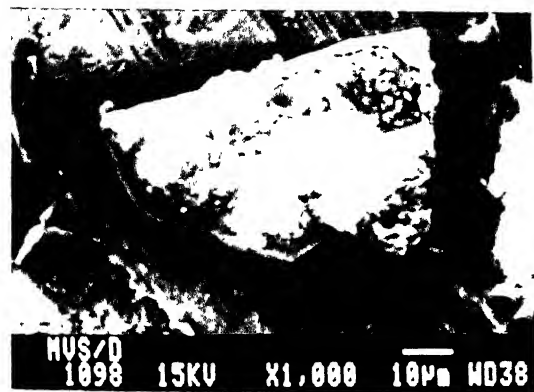


(e)

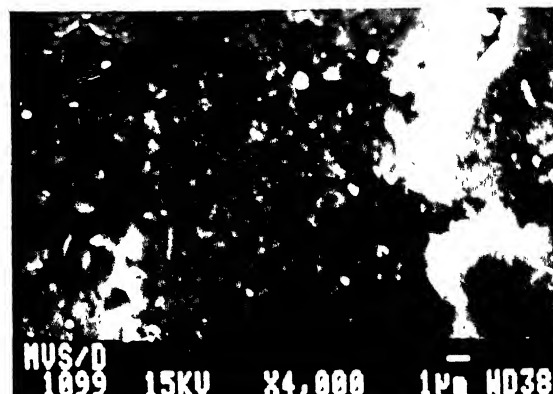


(c)

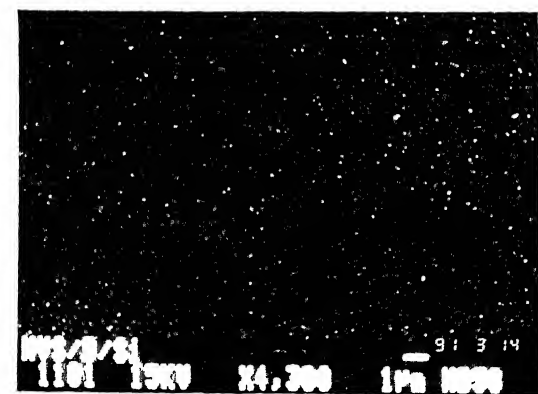
Fig. 2-1.4 X-ray mapping of sample C with a) micrograph, b) W, c) Si, d) Al, e) Fe distribution.



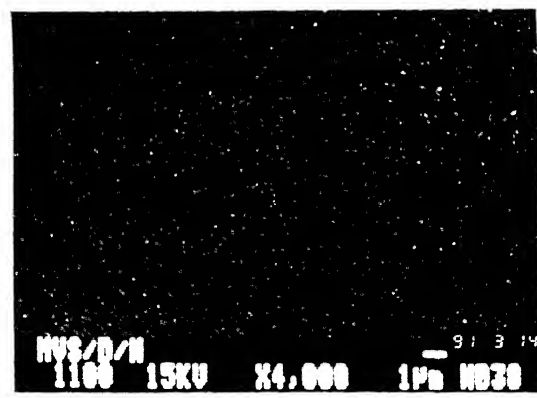
(a)



(b)



(c)



(d)

Fig. 2-1.5 X-ray mapping of sample D with a) & b) micrograph of particle, c) Si, d) W distribution.



## CHAPTER 3

### PREPARATION AND CHARACTERISATION OF SYNTHETIC SAMPLES

#### 3.1 DIFFERENT SAMPLES IN SERIES

There is a family of minerals which can be grouped as wolframite with hübnerite ( $\text{MnWO}_4$ ) and ferberite ( $\text{FeWO}_4$ ) as end members and with infinitely large number of intermediate ferrous manganous tungstate. Wolframite is considered as a mixture of ferrous and manganous tungstates 'containing not less than 20% and not more than 80% of either'[7]. Its general formula is  $(\text{Fe}_x\text{Mn}_{1-x})\text{WO}_4$  in which x varies between 0.2 to 0.8 and may be typically 0.5. We tried to obtain imitations of hübnerite, ferberite and wolframite with various proportion of iron and manganese. These seven theoretical composition are described in Table 3-1.

The weight percentage of Fe, Mn and W are calculated from molecular formula of  $(\text{Fe,Mn})\text{WO}_4$ .

Atomic weight of W = 183.85

Fe = 55.847

Mn = 54.938

#### 3.2 PREPARATION METHOD

##### 1) PRECIPITATION METHOD

First we tried the method in which solution of sodium tungstate was added to  $\text{MnSO}_4$  solution to give greyish precipitate

TABLE 3-1

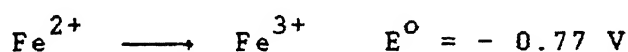
Sr. No.	Fe	Mn	Mol. Wt. (FeMn)WO <sub>4</sub>	Mol. Wt. without oxygen (FeMnW)	% Fe	% Mn	% W	Weight Ratio		Atomic Ratio		Wt % without oxygen		
								Fe/Mn	Fe/W	Fe/Mn	Fe/W	% Fe	% Mn	% W
1.	100	0	303.697	239.697	18.39	0	60.53	∞	0.303	∞	1	23.29	0	76.70
2.	80	20	303.515	239.515	14.72	3.62	60.57	4.06	0.243	4.0	0.8	18.65	4.58	76.75
3.	60	40	303.333	239.333	11.04	7.24	60.60	1.52	0.182	1.5	0.6	14.00	9.18	76.81
4.	50	50	303.242	239.242	9.20	9.05	60.62	1.01	0.151	1.0	0.5	11.67	11.48	76.84
5.	40	60	303.151	239.151	7.36	10.86	60.64	0.67	0.121	0.66	0.4	9.34	13.78	76.87
6.	20	80	302.969	238.969	3.68	14.50	60.68	0.25	0.060	0.25	0.2	4.67	18.39	76.93
7.	0	100	302.788	238.788	0	18.14	60.71	0.00	0.000	0.00	0.0	0.00	23.00	76.99

of  $\text{MnWO}_4$ . On heating to  $100^\circ\text{C}$ , it loses water and becomes pale yellow.

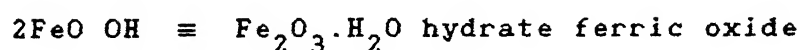
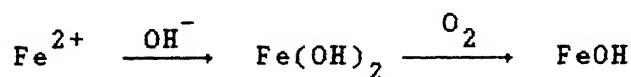
We used similar method for preparation of ferrous tungstate but failed to get  $\text{FeWO}_4$ ; the probable reason was as follows :

Manganese exists in +2 to +7 oxidation states in solution, with +2 being the most stable. Manganese (II) at ordinary concentrations is not hydrolyzed appreciably before precipitation occurs, but in alkaline medium it gets precipitated to  $\text{Mn(OH)}_2$  [6-a].

In case of iron, +2 and +3 oxidation states are stable over broad range of potential.



This is not a substantially high value. In presence of oxygen or other oxidising agents  $\text{Fe}^{2+}$  may be readily oxidized to  $\text{Fe}^{3+}$  [6-b].  $\text{Fe}^{2+}$  hydrolyzes to produce the array of mono nuclear species  $\text{FeOH}^+$  to  $\text{Fe(OH)}_4^{2-}$  between pH 7 and 14. In alkaline medium  $\text{Fe}^{2+} \xrightarrow{[\text{o}]}$   $\text{Fe}^{3+}$ .



In alkaline medium  $\text{Fe}^{3+}$  is more stable than  $\text{Fe}^{2+}$ .

For the formation of  $\text{FeWO}_4$  and  $\text{MnWO}_4$  we want stable ions  $\text{WO}_4^{2-}$ ,  $\text{Fe}^{2+}$  and  $\text{Mn}^{2+}$  in solution  $\text{WO}_4^{2-}$  is stable above pH 8 to 9. But

$\text{Fe}^{2+}$  gets hydrolysed and get oxidised to  $\text{Fe}^{3+}$  in alkaline medium. Therefore, we could not obtain  $\text{FeWO}_4$  by this method although we did get  $\text{MnWO}_4$ . Therefore we tried another method to prepare tungstates.

#### 11) HIGH TEMPERATURE FUSION METHOD

Wolframite series was prepared by fusion of  $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ ,  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$  and  $\text{MnCl}_2 \cdot 2\text{H}_2\text{O}$  at  $800^\circ\text{C}$  for 5 hrs. These salts were added according to their atomic proportions. These seven samples may be listed [7] :

TABLE 3-2

Sr.No.	Fe	Mn	$\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$	$\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$	$\text{Na}_2\text{WO}_4$
1	100	0	1.9881	0	3.2986
2	80	20	1.5905	0.3959	3.2986
3	60	40	1.1929	0.7917	3.2986
4	50	50	0.9941	0.9846	3.2986
5	40	60	0.7953	1.1875	3.2986
6	20	80	0.3976	1.5833	3.2986
7	0	100	0	1.9791	3.2986

This time we obtained  $\text{FeWO}_4$  and  $\text{MnWO}_4$  but X-ray diffraction pattern showed some extra peaks which were due to unreacted species like chlorine. To remove these we carried out boiling water treatment for half an hour. Satisfactorily we got all the X-ray peaks matching with the standard 'd' values showing the unreacted species removed. These seven samples were examined for X-ray, SEM and for chemical analysis.

### 3.3 CHARACTERISATION

#### 3.3.1 X-ray Analysis Report of the Series of Synthesized Samples

These seven samples were examined for X-ray diffraction. From X-ray diffraction pattern we calculated 'd' values and compared with standard 'd' values. Most of the peaks matched with those for standard sample. Some peaks of tungsten trioxide were also seen. In this chapter, 'd' values for 'wolframite' correspond to synthetic wolframite and not the mineral sample. The distinction between the two is brought out in Appendix. The standard 'd' value data for synthetic wolframite may be considered as 50:50 ferrous-manganese proportion.

SAMPLE 1

TABLE 3-3 [10]

Sr.No.	2 $\theta$	'd'	Standard 'd'	
1.	26.90	4.925		
2.	36.30	3.677 (59)	Wolframite	3.673
3.	45.40	2.968	Wolframite	2.968
4.	50.35	2.692 (60)	WO <sub>3</sub>	2.70
5.	54.30	2.510		
6.	62.50	2.208 (73)	Ferberite	2.194
7.	66.95	2.076	Wolframite	2.070
8.	77.00	1.840	Ferberite	1.823
9.	85.10	1.693 (48)	WO <sub>3</sub>	1.680
10.	91.45	1.599 (50)	Wolframite	1.594
11.	100.90	1.485		
12.	104.10	1.4576		

## SAMPLE 2

TABLE 3-4

Sr.No.	$2\theta$	'd'	Standard 'd'	
1.	13.40	9.817		
2.	23.00	5.745	Wolframite	5.730
3.	27.20	4.871 (100)		
4.	36.20	3.686 (67)	Wolframite	3.673
5.	45.70	2.949 (65)	Wolframite	2.946
6.	47.00	2.872	Wolframite	2.864
7.	50.30	2.695 (72)	WO <sub>3</sub>	2.70
8.	54.20	2.514		
9.	55.80	2.447	Wolframite	2.460
10.	56.70	2.412	Hübnerite	2.416
11.	62.60	2.20	Wolframite	2.202
12.	68.20	2.04	Wolframite	2.010
13.	69.20	2.017	Wolframite	2.010
14.	77.00	1.840	Wolframite	1.836
15.	80.10	1.780	Wolframite	1.775
16.	82.40	1.738	Wolframite	1.733
17.	85.20	1.692	Hübnerite	1.683
18.	89.10	1.632	Hübnerite	1.647
20.	100.90	1.485 (64)	Hübnerite	1.488

## SAMPLE 3

TABLE 3-5

Sr.No.	2θ	'd'	Standard 'd'	
1.	13.50	9.74		
2.	23.00	5.745	Wolframite	5.73
3.	27.40	4.836 (81)		
4.	32.80	4.057		
5.	36.20	3.686 (86)	Wolframite	3.673
6.	45.10	2.986		
7.	45.70	2.949 (65)	Wolframite	2.946
8.	47.00	2.872	Wolframite	2.864
9.	50.30	2.695	WO <sub>3</sub>	2.70
10.	54.80	2.489	Wolframite	2.488
11.	56.90	2.404 (94)	Wolframite	2.392
12.	62.60	2.204	Wolframite	2.202
13.	68.20	2.043	Wolframite	2.054
14.	69.30	2.014	Wolframite	2.010
15.	73.40	1.916	Wolframite	1.911
16.	74.90	1.883	Wolframite	1.881
17.	77.00	1.840	Wolframite	1.836
18.	80.10	1.780	Wolframite	1.775
19.	82.30	1.740	Wolframite	1.733
20.	83.30	1.723	Wolframite	1.729
21.	85.20	1.692	Ferberite	1.684
22.	91.00	1.605	Hübnerite	1.609
23.	91.70	1.596	Wolframite	1.594
24.	95.50	1.547	Hübnerite	1.550

contd...

Table 3-5 contd...

Sr.No.	2 $\theta$	'd'	Standard 'd'	
25.	97.50	1.523	Hübnerite	1.527
26.	98.80	1.508	Hübnerite	1.510
27.	99.80	1.497	Hübnerite	1.498
28.	100.90	1.485 (62.5)	Hübnerite	1.488

SAMPLE 4

TABLE 3-6

Sr.No.	2 $\theta$	'd'	Standard 'd'	
1.	23.00	5.745	Wolframite	5.73
2.	27.50	4.819		
3.	33.00	4.033		
4.	35.40	3.768	Wolframite	3.761
5.	36.20	3.686 (91)	Wolframite	3.673
6.	45.00	2.993 (61)		
7.	45.70	2.949 (69)	Wolframite	2.946
8.	46.90	2.878	Wolframite	2.864
9.	50.30	2.695		
10.	54.70	2.493 (62.5)	Wolframite	2.488
11.	56.80	2.408 (71.5)	Wolframite	2.392
12.	62.00	2.224	Wolframite	2.217
13.	62.70	2.202	Wolframite	2.202
14.	68.10	2.046	Wolframite	2.054
15.	69.20	2.017	Wolframite	2.023

contd...



Table 3-6 contd...

Sr.No.	2 $\theta$	'd'	Standard 'd'
16.	73.40	1.917	Wolframite 1.911
17.	74.90	1.884	Wolframite 1.881
18.	76.90	1.842	Wolframite 1.836
19.	84.90	1.782	Wolframite 1.775
20.	82.20	1.742	Wolframite 1.733
21.	83.20	1.725	Wolframite 1.729
22.	83.60	1.718	Wolframite 1.719
23.	85.00	1.694	Hübnerite 1.680
24.	86.10	1.677	Hübnerite 1.677
25.	90.90	1.607	Hübnerite 1.609
26.	91.5	1.595	Wolframite 1.594
27.	95.5	1.547	Hübnerite 1.550

SAMPLE 5

TABLE 3-7

Sr.No.	2 $\theta$	'd'	Standard 'd'
1.	23.00	5.745	Wolframite 5.73
2.	27.50	4.819 (98)	
3.	35.40	3.767	Wolframite 3.761
4.	36.20	3.686 (43)	
5.	45.10	2.986 (61.5)	
6.	45.80	2.943 (75)	Wolframite 2.946
7.	46.90	2.878	Wolframite 2.864
8.	50.30	2.695	

contd...

Table 3-7 contd...

Sr.No.	2 $\theta$	'd'	Standard 'd'
9.	54.70	2.493	Wolframite 2.488
10.	56.70	2.412 (36)	Hübnerite 2.416
11.	61.80	2.230	Wolframite 2.217
12.	62.60	2.204	Wolframite 2.202
13.	68.10	2.045	Wolframite 2.054
14.	69.20	2.0172	Wolframite 2.023
15.	75.80	1.864	Ferberite 1.873
16.	77.70	1.8260	Wolframite 1.836
17.	80.90	1.765	Wolframite 1.775
18.	82.70	1.733	Wolframite 1.733
19.	83.20	1.725	Wolframite 1.729
20.	84.30	1.706	Wolframite 1.719
21.	84.40	1.7052	Wolframite 1.719
22.	86.00	1.679	WO <sub>3</sub> 1.680
23.	92.40	1.587	Wolframite 1.594
24.	98.20	1.515	Hübnerite 1.5100
25.	101.70	1.477	Hübnerite 1.4754

SAMPLE 6

TABLE 3-8

Sr.No.	2 $\theta$	'd'	Standard 'd'
1.	23.00	5.745 (84)	Wolframite 5.73
2.	27.50	4.819	
3.	35.40	3.767	Wolframite 3.761

contd...

Table 3-8 contd...

Sr.No.	2 $\theta$	'd'	Standard	'd'
4.	36.10	3.696 (54)	Hübnerite	3.700
5.	45.00	2.993 (77)	Hübnerite	2.996
6.	45.80	2.943 (97)	Wolframite	2.946
7.	46.90	2.878	Hübnerite	2.880
8.	50.30	2.700	WO <sub>3</sub>	2.70
9.	54.70	2.493 (44)	Hübnerite	2.497
10.	56.80	2.408	Hübnerite	2.416
11.	61.90	2.227	Hübnerite	2.237
12.	62.60	2.204	Wolframite	2.202
13.	66.80	2.080	Hübnerite	2.087
14.	68.10	2.045	Wolframite	2.054
15.	69.20	2.017	Wolframite	2.023
16.	73.40	1.916	Wolframite	1.911
17.	74.90	1.883	Wolframite	1.881
18.	76.60	1.848	Wolframite	1.836
19.	80.00	1.782	Hübnerite	1.784
20.	82.20	1.742	Hübnerite	1.744
21.	83.30	1.723	Hübnerite	1.726
22.	83.60	1.718	Hübnerite	1.7196
23.	90.80	1.608	Hübnerite	1.609
24.	91.50	1.599	Hübnerite	1.5996
25.	95.40	1.548	Hübnerite	1.550
26.	97.40	1.524	Hübnerite	1.527
27.	98.80	1.508	Hübnerite	1.5023
28.	99.70	1.498	Hübnerite	1.4981
29.	100.80	1.486	Hübnerite	1.475

## SAMPLE 7

TABLE 3-9

Sr.No.	2 $\theta$	'd'	Standard 'd'	
1.	23.00	5.75	Hübnerite	5.76
2.	27.20	4.87 (77)	Hübnerite	4.84
3.	35.50	3.757	Hübnerite	3.78
4.	36.20	3.687 (41)	Hübnerite	3.70
5.	45.20	2.981	Hübnerite	2.996
6.	45.80	2.944	Hübnerite	2.95
7.	47.00	2.873	Hübnerite	2.88
8.	50.00	2.710 (41)	WO <sub>3</sub>	2.70
9.	55.30	2.468 (28)	Hübnerite	2.474
10.	56.70	2.412 (69)	Hübnerite	2.416
11.	62.10	2.221	Hübnerite	2.237
12.	62.70	2.202	Hübnerite	
13.	69.80	2.002		
14.	73.30	1.919	Hübnerite	1.921
15.	76.80	1.844	Hübnerite	1.85
16.	80.00	1.782	Hübnerite	1.784
17.	82.30	1.741	Hübnerite	1.744
18.	83.40	1.722	Hübnerite	1.719
19.	87.20	1.661	Hübnerite	1.65
20.	90.80	1.608	Hübnerite	1.609
21.	97.70	1.5212	Hübnerite	1.5221
22.	99.30	1.503	Hübnerite	1.5023
23.	100.70	1.487	Hübnerite	1.488

### 3.3.2 Chemical Analysis Report on the Synthesized Series of Wolframite Samples

#### a) Determination of Fe [5]

Method: 0.2 gms of sample was dissolved in 15 ml HCl and heated for 20 minutes. After adding water, the solution was filtered. The filtrate was boiled again and  $\text{SnCl}_2$  was added till it becomes colourless. After cooling the solution 10 ml  $\text{MgCl}_2$  and 20 ml of acid mixture was added. Titration was carried out with potassium dichromate using diphenyl amine as a indicator.

#### b) Determination of $\text{WO}_3$ (Gravimetry) [4]

0.2 gm sample was dissolved in mixture of hydrochloric acid and nitric acid (10-15 ml each), and baked for 3 hours. Water was added and while boiling 10 ml of cinchlorine hydrochloride solution was added. After that it was digested for 2 hours and then filtered. The precipitate was washed 3 times with 0.1% cinchlorine hydrochloride solution. The precipitate was ignited in a weighed platinum crucible. Temperature should not exceed  $750^\circ\text{C}$  ( $\text{WO}_3$  is volatile above this temperature). The residue was of lemon yellow colour and then weighed with crucible.

$$\text{WO}_3\% = \frac{\text{wt. of ignited residue}}{\text{wt. of material taken}} \times 100$$

c) **Determination of Mn by Spectrophotometer**

Method : 0.1 gm sample was dissolved in a beaker containing mixture of hydrochloric, sulphuric and nitric acid (10 ml each) and baked for 3 hours. It was again refluxed with 2-5 ml of  $\text{H}_2\text{SO}_4$ . By adding water and little  $\text{HNO}_3$ , it was again boiled and then filtered.

The filtrate was taken and made upto 100 ml. From that 10 ml was taken and made it 100 ml. Again from that 10 ml of solution was taken for analysis. To this 15-20 ml conc.  $\text{HNO}_3$  and 5-10 ml of orthophosphoric acid was added and heated. 0.2 to 0.3 gm of potassium periodate was added while boiling till all reagents got dissolved.

After developing colour it was made upto 100 ml and absorbance was measured in spectrophotometer.

For calibration, 0.1 gm of pure manganese metal was dissolved in 10 ml  $\text{HNO}_3$ . The volume was made upto 250 ml. From that 5 ml solution was taken and made it 100 ml by adding water. From 100 ml solution, 5 ml, 10 ml, 15 ml and 20 ml were taken in separate beaker. The sample which was taken for analysis was treated among these solutions and their absorbance was measured. The graph was plotted between concentration and absorbance. From that concentration of manganese of synthesized sample was calculated.

TABLE 3-10

Sample	% Mn	Fe %	WO <sub>3</sub> %
1	0.0	67.2	11.65
2	14.2	30.8	44.7
3	15.6	17.08	58.3
4	18.0	14.84	62.15
5	17.0	11.76	22.0
6	18.7	7.26	65.36
7	20.0	0.0	71.0

### 3.3.3 Elemental Analysis of Synthesized Samples on Scanning Electron Microscope

These seven synthesized samples were examined under SEM. The elemental analysis showed that Fe:Mn ratios were nearly the expected proportions. Also because of heterogeneity we were having different proportions of Fe:Mn at different positions.

Initially chlorine was found present and later removed by acidification treatment in which the sample was heated with water for half an hour. The result showed that chlorine was almost removed. Also X-ray diffraction pattern of these samples shows most of the peaks matching with standard sample.

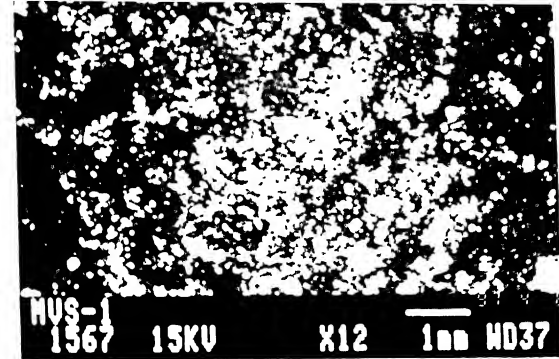
The photomicrographs of these seven samples shows heterogeneous mass and not homogeneous mass. The photomicrograph shows the overall area where bulk analysis was done. And this analysis comes out on EDAX system attached to the scanning electron microscope.

## SEM ANALYSIS FIGURES FOR SYNTHETIC WOLFRAMITE

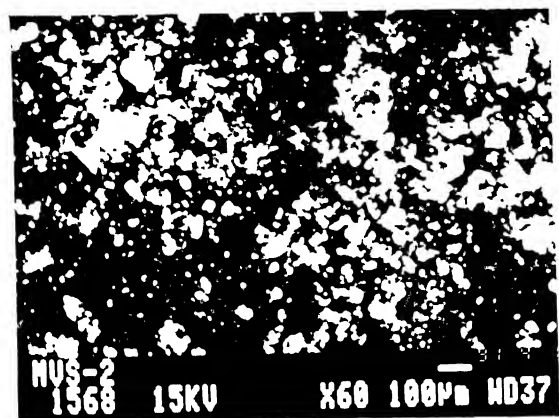
TABLE 3-11

$\text{Fe}_x\text{Mn}_{1-x}(\text{WO}_4)$ Sample No.	Value of x	SEM analysis wt. % (oxygen free basis)			SEM Analysis Atomic ratio	
		Fe	Mn	W	Fe/Mn	Fe/W
1	1	55.74	0	44.25	-	4.14
2	0.8	32.82	7.92	59.26	4.07	1.82
3	0.6	19.22	9.42	71.36	2.005	0.88
4	0.5	14.37	12.54	73.08	1.12	0.64
5	0.4	9.39	14.39	75.66	0.61	0.40
6	0.2	6.49	21.64	71.88	0.29	0.297
7	0	0	43.29	56.71	0	0

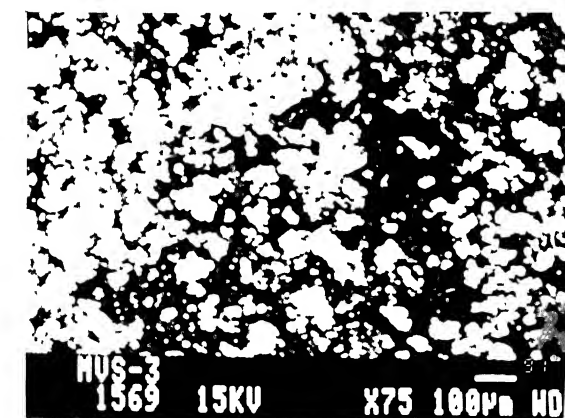




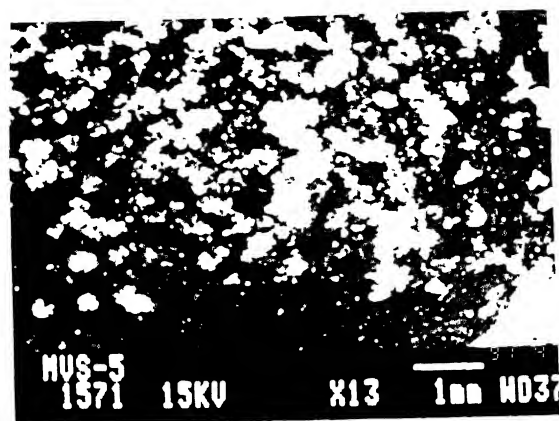
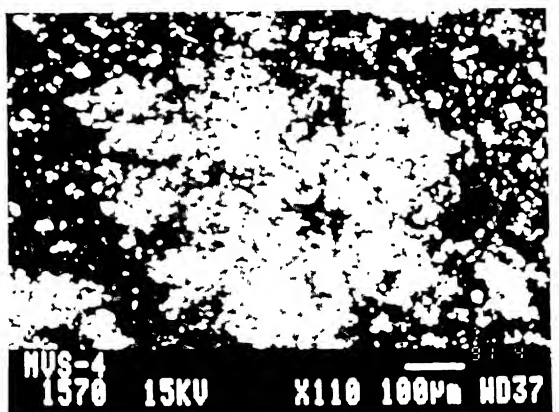
1



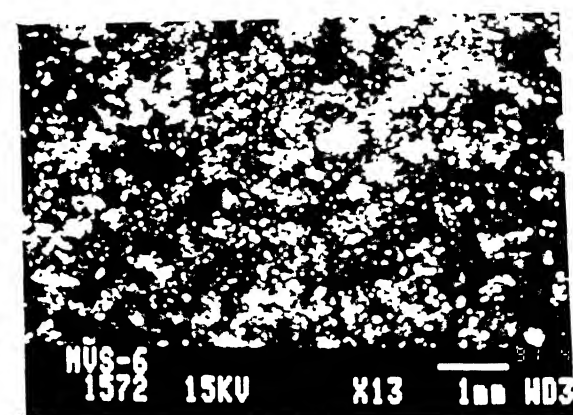
2



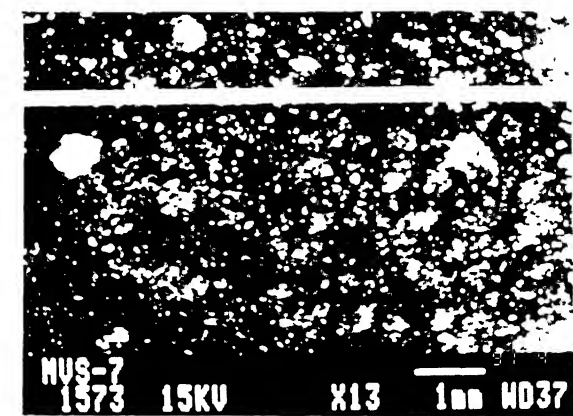
3



5



6



7

Fig. 3-1.1 : Photomicrographs of synthetic samples 1,2,3,4,5,6,7.

## CHAPTER 4

### LEACHING STUDIES ON THE SYNTHESIZED SAMPLES OF WOLFRAMITE

4.1 In tungsten extraction, hydrometallurgy plays an important role on account of its extremely high melting point. The main objective of tungsten extraction is to convert the tungsten contained in the ore concentrate to an intermediate compound viz. tungstic acid or ammonium paratungstate which can be reduced to yield metallic tungsten in subsequent reduction process [8].

Of the many methods employed or prepared for the decomposition of tungsten ores, only 3 are of commercial importance [9]

- i) digestion with acids (usually HCl)
- ii) digestion with alkalies
- iii) fusion with alkali and alkali salts.

Acid digestion is usually applied only to scheelite since minerals of wolframite are comparatively resistant to attack by acids. Ores containing wolframite mineral are ordinarily decomposed by digestion with a strong (50%) solution of alkali metal hydroxide either under pressure or simply by boiling at atmospheric pressure.

One of our objectives was to study selectivity in the leaching of tungsten ore. Leaching of wolframite can be done by NaOH or  $\text{Na}_2\text{CO}_3$ . But we were basically interested in understanding the NaOH interaction on wolframite. We were also interested in

kinetics of leaching process. So we carried out leaching of these synthesized samples with alkali and alkali salts and then studied the solid residue using SEM, X-ray diffraction and chemical analysis.

We have carried out leaching techniques of three samples for various time limits.

- i)  $\text{FeWO}_4$
- ii)  $(\text{Fe}, \text{Mn})\text{WO}_4$
- iii)  $\text{MnWO}_4$

For  $(\text{Fe}, \text{Mn})\text{WO}_4$  samples, 10 leaching experiments were carried out by NaOH and NaCl for time limits upto 15 minute, 30 minute, 1 hour, 2 hour and 4 hour. Also for the same sample 5 more experiments were carried out at higher temperatures ( $86-88^\circ\text{C}$ ).

For  $\text{FeWO}_4$  and  $\text{MnWO}_4$  samples, 5 leaching experiments for each were carried out for the same time limit.

Leaching set up was as follows -

0.5 gm sample was dissolved in 250 ml of 1N NaOH solution in beaker. This beaker, in turn, was placed in a glass vessel containing hot water. The temperature of water was controlled by heating tape surrounding the vessel. Thermometer was dipped in water. The heating tape was connected to dimmerstat. The vessel containing beaker was placed on magnetic stirrer. So the solution was simultaneously heated and magnetically stirred.

The temperature of water bath was maintained at  $90^{\circ}\text{C}$ . The temperature of the solution in beaker varied from  $80$  to  $85^{\circ}\text{C}$ . All the leaching experiments were carried out in similar way. The solid residue was filtered and dried and taken for observation.

Leaching of  $(\text{Fe,Mn})\text{WO}_4$  was carried out with  $\text{NaCl}$  and  $\text{NaOH}$  solution. To find out by which method it is more leachable, chemical analysis of two samples were carried out. The sample of 50:50) ferrous to manganous ratio was leached with  $\text{NaOH}$  and  $\text{NaCl}$  for 30 minutes. By chemical analysis, the  $\text{WO}_3$  content dissolved in  $\text{NaOH}$  was found to be more than  $\text{WO}_3$  content dissolved in  $\text{NaCl}$  solution. The amount of tungsten oxide dissolved out of 0.5 gm sample (assaying 62.15%  $\text{WO}_3$ ) in 1N  $\text{NaOH}$  solution was 0.07975 gm in 250 c.c. or 0.319 gm/litre corresponding to a recovery of 25.66%. Under identical condition,  $\text{NaCl}$  dissolution resulted in 8.37% recovery. On the basis of this result, we carried out our subsequent leaching experiments with  $\text{NaOH}$  solution only, considering  $\text{NaOH}$  solution to be the better of two.

#### 4.2 X-RAY DIFFRACTION STUDIES OF SOLID RESIDUE

The solid residue obtained from various leaching experiments were examined for X-ray diffraction. The X-ray diffraction pattern shows the new phase i.e. some peaks of sodium tungstate and 'd' values obtained were matching with standard 'd' values.

X-RAY DIFFRACTION PATTERN OF SAMPLE  $\text{FeWO}_4$  AFTER LEACHING  
WITH SODIUM HYDROXIDE SOLUTION.

a) For 15 minutes.

TABLE 4-1

Sr.No.	$2\theta$	'd'	Standard 'd'
1	13.35	9.85	
2	13.50	9.74	
3	23.20	5.69	
4	27.0	4.90	
5	35.7	3.736	Ferberite 3.745
6	36.4	3.66	Wolframite 3.673
7	45.1	2.986	Sodium tungstate 2.988
8	45.6	2.955	Wolframite 2.946
9	47.4	2.899	Sodium tungstate 2.898
10	50.5	2.685	Sodium tungstate 2.684
11	54.4	2.505	
12	55.4	2.464	Ferberite 2.474

b) For 30 minutes

TABLE 4-2

Sr.No.	$2\theta$	'd'	Standard 'd'
1	13.5	9.74	
2	23.25	5.68	
3	26.9	4.924	
4	35.8	3.726	

contd...

Table 4-2 contd...

Sr.No.	2θ	'd'	Standard 'd'
5	36.4	3.667	Wolframite 3.673
6	45.5	2.962	Wolframite 2.968
7	47.4	2.849	Ferberite 2.856
8	50.5	2.685	Sodium tungstate 2.684
9	55.4	2.505	
10	55.5	2.460	Ferberite 2.474
11	61.0	2.256	
12	62.8	2.198	Ferberite 2.194

c) For 1 hour

TABLE 4-3

Sr.No.	2θ	'd'	Standard 'd'
1	26.2	5.053	
2	35.8	3.726	
3	36.3	3.677	Wolframite 3.673
4	45.4	2.968	Wolframite 2.968
5	47.3	2.855	Ferberite 2.856
6	50.4	2.690	Sodium tungstate 2.684
7	54.4	2.505	
8	55.3	2.468	Ferberite 2.474

d) For 2 hour

TABLE 4-4

Sr.No.	$2\theta$	'd'	Standard 'd'
1	13.2	9.96	
2	26.9	4.924	
3	35.8	3.726	
4	36.4	3.667	Wolframite 3.673
5	45.5	2.962	Wolframite 2.968
6	47.4	2.849	Ferberite 2.856
7	50.5	2.685	Sodium tungstate 2.684
8	54.3	2.510	
9	55.3	2.468	Ferberite 2.474

e) For 4 hour

TABLE 4-5

Sr.No.	$2\theta$	'd'	Standard 'd'
1	26.9	4.924	
2	35.7	3.736	Ferberite 3.745
3	36.3	3.677	Wolframite 3.673
4	45.0	2.993	Sodium tungstate 2.988
5	45.6	2.955	Ferberite 2.940
6	50.3	2.695	Sodium tungstate 2.684
7	54.2	2.514	
8	55.2	2.472	Sodium tungstate 2.475
9	62.7	2.201	Ferberite 2.194

X-RAY DIFFRACTION PATTERN OF  $\text{FeMn}(\text{WO}_4)_2$  AFTER LEACHING WITH NaOH.

a) For 15 minutes

TABLE 4-6

Sr.No.	$2\theta$	'd'	Standard 'd'
1	27.0	4.906	
2	27.7	4.785	Wolframite 4.780
3	35.5	3.757	Wolframite 3.761
4	36.3	3.677	Wolframite 3.673
5	45.1	2.986	Sodium tungstate 2.988
6	45.7	2.949	Wolframite 2.946
7	47.0	2.872	Wolframite 2.864
8	50.4	2.690	Sodium tungstate 2.684
9	54.3	2.510	
10	54.8	2.489	Wolframite 2.488
11	56.8	2.408	Hübnerite 2.416
12	62.0	2.224	Wolframite 2.217
13	62.8	2.198	Wolframite 2.202
14	67.2	2.069	Wolframite 2.069

b) For 30 minutes

TABLE 4-7

Sr.No.	$2\theta$	'd'	Standard 'd'
1	27.7	4.785	Wolframite 4.780
2	35.6	3.747	Wolframite 3.761
3	36.3	3.677	Wolframite 3.673
4	45.1	2.986	Sodium tungstate 2.988

contd...



Table 4-7 contd...

Sr.No.	2 $\theta$	'd'	Standard 'd'
5	45.9	2.937	Wolframite 2.946
6	47.0	2.872	Wolframite 2.864
7	50.4	2.700	WO <sub>3</sub> 2.700
8	54.3	2.510	
9	54.9	2.484	Wolframite 2.488
10	56.9	2.404	Hübnerite 2.416

c) For 1 hour

TABLE 4-8

Sr.No.	2 $\theta$	'd'	Standard 'd'
1	27.0	4.90	
2	27.7	4.177	
3	35.7	3.736	Ferberite 3.745
4	36.2	3.686	Wolframite 3.673
5	45.1	2.986	Sodium tungstate 2.988
6	45.9	2.937	Wolframite 2.946
7	47.0	2.872	Wolframite 2.864
8	50.4	2.690	Sodium tungstate 2.684
9	54.3	2.510	
10	55.0	2.480	Wolframite 2.488
11	57.0	2.400	

d) For 2 hours

TABLE 4-9

Sr.No.	$2\theta$	'd'	Standard 'd'
1	13.4	9.817	
2	23.1	5.72	Wolframite 5.73
3	27.0	4.906	
4	27.5	4.819	
5	35.7	3.736	
6	36.2	3.686	Wolframite 3.673
7	45.1	2.986	Sodium tungstate 2.985
8	45.9	2.937	Wolframite 2.946
9	47.1	2.866	Wolframite 2.864
10	50.4	2.690	Sodium tungstate 2.684
11	54.8	2.489	Wolframite 2.488
12	57.0	2.400	Wolframite 2.392
13	62.8	2.198	Wolframite 2.202

e) For 4 hours

TABLE 4-10

Sr.No.	$2\theta$	'd'	Standard 'd'
1	23.0	5.745	Wolframite 5.73
2	27.0	4.906	
3	27.6	4.802	
4	35.5	3.757	Wolframite 3.761

contd...

Table 4-10 contd...

Sr.No.	2θ	'd'	Standard 'd'
5	36.2	3.686	Wolframite 3.673
6	45.0	2.993	Sodium tungstate 2.988
7	45.8	2.943	Wolframite 2.946
8	47.0	2.872	Wolframite 2.864
9	50.4	2.690	Sodium tungstate 2.684
10	54.4	2.505	
11	54.9	2.484	Wolframite 2.488
12	56.8	2.408	

X-RAY DIFFRACTION PATTERN OF SAMPLE  $MnWO_4$  AFTER LEACHING WITH  
WITH NaOH

a) For 15 minutes.

TABLE 4-11

Sr.No.	2θ	'd'	Standard 'd'
1	27.7	4.785	Sodium tungstate 4.78
2	35.6	3.747	
3	36.4	3.667	
4	45.2	2.980	Hübnerite 2.996
5	45.8	2.943	Hübnerite 2.954
6	47.2	2.861	
7	50.1	2.705	$WO_3$ 2.70
8	54.9	2.484	Hübnerite 2.474
9	55.3	2.468	Hübnerite 2.474
10	56.8	2.408	Hübnerite 2.416

b) For 30 minutes.

TABLE 4-12

Sr.No.	2 $\theta$	'd'	Standard 'd'	
1	22.8	5.795		
2	27.45	4.827		
3	35.4	3.767		
4	36.1	3.696	Hübnerite	3.70
5	44.9	2.999	Hübnerite	2.996
6	46.7	2.890	Hübnerite	2.880
7	49.8	2.720		
8	54.5	2.500	Sodium tungstate	2.497
9	55.2	2.472	Hübnerite	2.474
10	56.7	2.4122	Hübnerite	2.416

c) For 1 hour.

TABLE 4-13

Sr.No.	2 $\theta$	'd'	Standard 'd'	
1	23.0	5.74		
2	27.6	4.802		
3	35.4	3.767	Hübnerite	3.78
4	36.2	3.686	Hübnerite	3.70
5	45.1	2.986	Hübnerite	2.996
6	45.8	2.943	Hübnerite	2.954
7	47.1	2.865	Hübnerite	2.880
8	50.1	2.705	WO <sub>3</sub>	2.70
9	54.8	2.489	Hübnerite	2.497
10	55.2	2.472	Hübnerite	2.474

d) For 2 hours.

TABLE 4-14

Sr.No.	2 $\theta$	'd'	Standard 'd'	
1	23.1	5.72		
2	27.7	4.78	Sodium Tungstate 4.78	
3	35.5	3.75		
4	36.3	3.677		
5	45.2	2.980	Hübnerite	2.996
6	45.7	2.949	Hübnerite	2.95
7	47.0	2.872	Hübnerite	2.88
8	50.0	2.710	WO <sub>3</sub>	2.700
9	54.8	2.489	Hübnerite	2.497
10	56.8	2.40	Hübnerite	2.416

#### 4.3 ELEMENTAL ANALYSIS OF LEACHED SYNTHETIC SAMPLES OF WOLFRAMITE ON SEM

The elemental analysis shows the dissolution of tungsten in NaCl and NaOH solution. From the results obtained, we had found that there was more dissolution of tungsten in NaOH solution than in NaCl solution.

I)  $\text{FeWO}_4$  LEACHED WITH  $\text{NaOH}$  SOLUTION

TABLE 4-15

Time	Weight %		Atomic %		Atomic Fe/W
	Fe	W	Fe	W	
0	55.74	44.26	80.57	19.43	4.14 (1)*
15 min.	86.73	13.27	95.56	4.44	21.5 (5.25)
30 min.	78.82	21.18	92.45	7.55	12.2 (3.00)
1 hr.	91.33	8.67	97.20	2.80	34.7 (8.4)
2 hr.	82.51	17.49	93.95	6.05	15.52 (3.7)
4 hr.	8.58	91.42	23.61	76.39	0.309

\* ( ) Figures in bracket indicate normalised values.

From the above table we can conclude that atomic ratio of Fe/W goes up much above unity, the highest value recorded is 34.7 indicating preferential dissolution of tungsten. Actually the Fe/W ratio goes up and down indicating steps of dissolution of successive layers.

II)  $(\text{Fe}, \text{Mn})\text{WO}_4$  LEACHED WITH  $\text{NaCl}$  AND  $\text{NaOH}$  SOLUTION.

Time	Weight %			Atomic %			Atomic Ratio		
	Fe	Mn	W	Fe	Mn	W	Fe/Mn	Fe/W	Mn/W
0	32.47	19.06	48.48	48.77	29.1	22.12	1.67(1)*	2.20(0.5)	1.31(0.5)
NaCl									
15 min.	34.63	18.36	47.01	51.25	27.62	21.13	1.85(1.1)	2.42(0.5)	1.30(0.5)
30 min.	33.45	13.81	52.74	52.67	22.10	25.23	2.38(1.4)	2.08(0.4)	0.87(0.3)
1 hr.	40.44	17.64	41.79	56.74	25.16	17.81	2.25(1.3)	3.18(.72)	1.41(0.5)
2 hr.	33.22	17.26	49.52	50.48	26.67	22.85	1.89(1.1)	2.2 (0.5)	1.16(0.4)
4 hr.	40.1	17.36	42.54	56.74	24.98	18.28	2.27(1.3)	3.10(0.7)	1.36(0.5)

	Weight %			Atomic %			Atomic Ratio		
	Fe	Mn	W	Fe	Mn	W	Fe/Mn	Fe/W	Mn/W
in.	48.61	18.04	33.35	63.06	23.79	13.15	2.65(1.6)	4.79(1.0)	1.80(0.7)
in.	45.02	17.61	37.37	60.62	24.10	15.28	2.51(1.2)	3.96(0.9)	1.57(0.7)
.	37.92	19.06	43.01	53.89	27.54	18.57	1.95(1.1)	2.9 (.65)	1.48(0.6)
.	44.77	16.20	39.03	61.25	22.53	16.22	2.71(1.6)	3.77(0.8)	1.39(0.5)
.	36.08	19.49	44.43	51.99	28.56	19.45	1.82(1.0)	2.67(0.6)	1.46(0.5)

) Figures in bracket indicate normalised values.

The above table shows that Fe/W ratio tends to remain what steady in the case of NaCl indicating non-selective solution; Fe/W ratio does not go up as much as in case of  $\text{FeWO}_4$  system. There are fluctuations in the ratio as functions of time; both the Fe/Mn and Fe/W ratios are slightly higher for the NaOH system than NaCl system.

The role of manganese seems to lower selectivity and bring Fe/W ratio in the solid close to the original value. Fe/W ratio is however always larger than Mn/W ratio.

III)  $\text{MnWO}_4$  LEACHED WITH NaOH SOLUTION.

TABLE 4-17

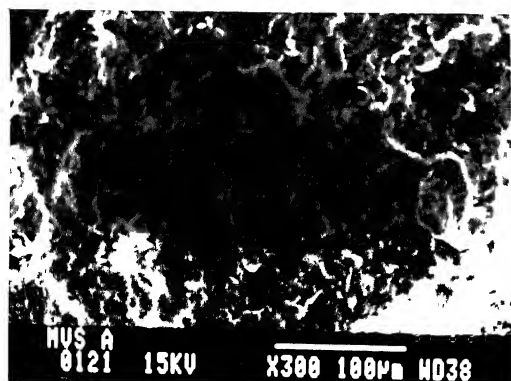
Time	Weight %		Atomic %		Atomic Mn/W
	Mn	W	Mn	W	
0	48.28	51.72	75.75	24.25	3.12 (1) <sup>*</sup>
15 min.	47.68	52.32	75.30	24.70	3.04 (0.977)
30 min.	49.89	50.11	76.91	23.09	3.33 (1.067)
1 hr.	39.96	60.04	69.01	30.99	2.22 (0.713)
2 hr.	54.06	45.94	79.75	20.25	3.93 (1.26)
4 hr.	52.21	47.79	78.52	21.48	3.655 (1.17)

\* ( ) Figures in bracket indicate normalised values.

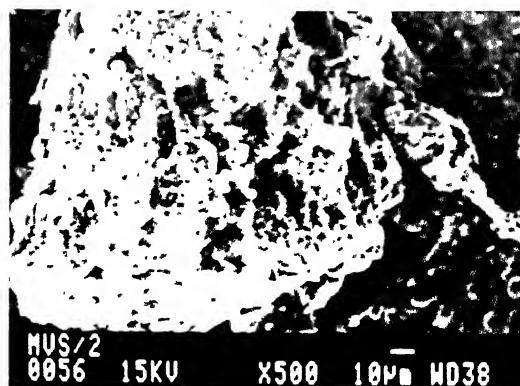
Whereas ferberite residue show Fe/W ratio much higher than that in the original, hübnerite clearly corresponds to non-selective leaching. The Mn/W ratio remains very close to unity (0.713 - 1.26).

The photomicrographs of few leached samples are as follows :

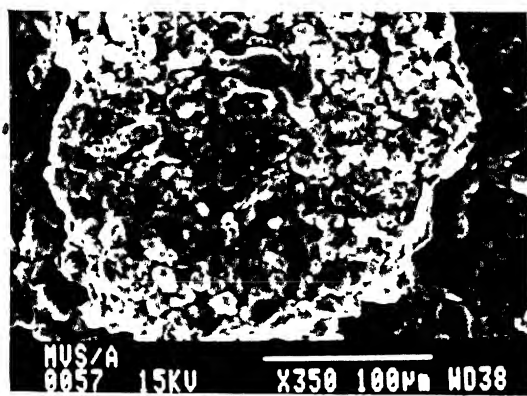




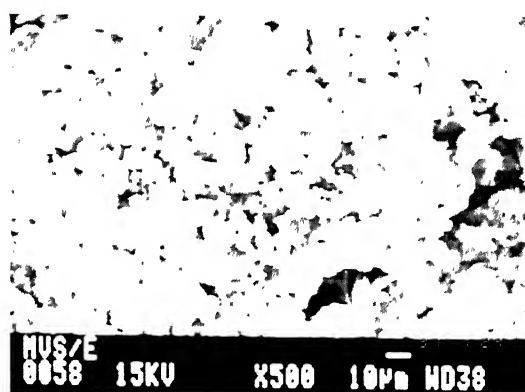
(a)



(b)

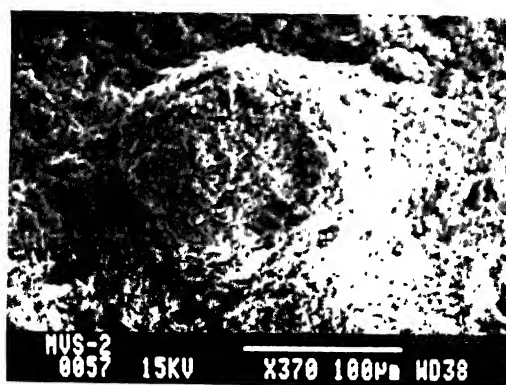


(c)

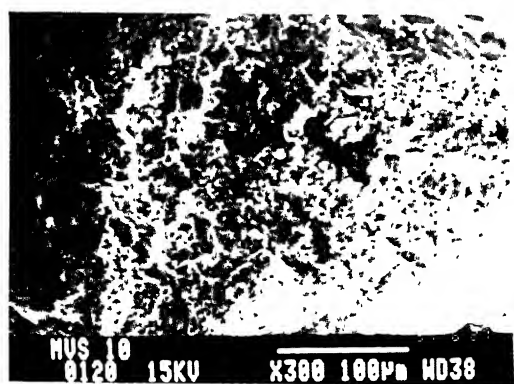


(d)

Fig. 4-1.1 : Photomicrographs of leached samples for  $\text{FeWO}_4$  a) for 15 min, b) for 4 hr. and for  $\text{MnWO}_4$  c) for 15 min, d) for 4 hr.



(a)



(b)

Fig. 4-1.2 Photomicrograph of leached sample for  $(\text{Fe}, \text{Mn})\text{WO}_4$   
a) for 15 min, b) for 4 hr.

#### 4.4 CHEMICAL ANALYSIS OF SYNTHESIZED SAMPLES AFTER LEACHING WITH NaOH SOLUTION

Chemical analysis of leached samples were carried out by same process as in chapter 3. The recovery of  $WO_3$  content, dissolved in NaOH solution at  $80^\circ C$  was determined by method described in 3.3.2. The recovery of  $WO_3$  content was calculated for three samples  $FeWO_4$ ,  $(Fe,Mn)WO_4$  and  $MnWO_4$  at various time limits. The analytical work is incomplete, and only a few results are presented.

TABLE 4-18

Time	$FeWO_4$	$(Fe,Mn)WO_4$	$MnWO_4$
30 min.	28.62	25.66	50.15
1 hr.	48.57	25.42	53.38

The iron dissolved in solution was also estimated by the process described in 3.3.2. The potassium dichromate solution used for titration was of 0.1N concentration. The following table shows iron percentage dissolved in solution.

TABLE 4-19

Time	$FeWO_4$	$(Fe,Mn)WO_4$
15 min.	4.77	12.03
30 min.	1.12	-

## CHAPTER 5

### DISCUSSION AND CONCLUDING REMARKS

The main objectives in our project have been to characterise the Indian wolframite ore and the series of synthesized wolframites and to study the alkali-leaching properties of the latter. Some of the tentative conclusions reached are as follows:

1. Tungsten is associated with quartz matrix and the chief gangue minerals are hematite, graphite, mica, arsenopyrite, ilmenite and chalcopyrite.
2. The magnetic properties of the two (out of four) specially separated fractions (A and D) may be attributed to ilmenite and wolframite contents.
3. In the four fractionated products (A-D), the  $\text{SiO}_2$  percentage varies from 25 to 60 p.c., iron 1-8 p.c., manganese below 0.2 p.c.,  $\text{WO}_3$  content 0.03-0.07 p.c. As per SEM analysis, the more abundant elements in the tungsten-rich areas (tungsten atomic p.c. 18.8 in 'A' and 25.3 in 'D') are Si, Fe, Al and W; the rest are Ti, Ca, Mn, Ba and Mg.
4. The above data as well as the SEM analysis show that tungsten is associated chiefly with iron and much less with calcium or manganese. Thus, we have in the ore high-iron low-manganese wolframite and some scheelite.
5. The X-ray mapping in SEM shows intimate dispersion of W, Fe and Mn in the quartz matrix. This suggests that preliminary

liberation and magnetic separation should be followed by more drastic hydrometallurgical steps.

6. Wolframite samples of graded composition were synthesized. Seven samples of  $\text{Fe}_x\text{Mn}_{1-x}(\text{WO}_4)$  were designed to have values of  $x$  varying from 1 (ferberite) to 0.8, 0.6, 0.5 (conventionally named as 'wolframite' with equal atomic proportion of Fe and Mn), 0.4, 0.2 and zero (hübnerite).

The standard literature data (vide appendix) were carefully examined. The crystals of the wolframite family are all monoclinic. Mellor [7] has summarised the various data. Ferberite has a greater tendency to form well-defined crystals-wedge-shaped, rhomboidal or cuboidal; the values of  $a$ ,  $b$ ,  $c$  and  $\beta$  are respectively  $4.70 \text{ \AA}^\circ$ ,  $5.69 \text{ \AA}^\circ$ ,  $4.93 \text{ \AA}^\circ$  and  $90^\circ$ . With increasing proportion of manganese, the lattice parameters systematically increase and  $\beta$  decreases indicating more open and less compact structure as macroscopically reflected by lower density (ferberite 7.61 and hübnerite 7.18). This phenomenon can be explained in terms of lower ionic radius of  $\text{Fe}^{2+}$  ( $0.75 \text{ \AA}^\circ$ ) than of  $\text{Mn}^{2+}$  ( $0.80 \text{ \AA}^\circ$ ).

Our data confirm the systematic gradation. Our ferberite sample showed  $2.94 \text{ \AA}^\circ$  'd' value for the  $(11\bar{1})$  plane. The corresponding values are 2.95 (synthetic wolframite), 2.953 (natural wolframite) and 3.00 for our hübnerite sample. Similarly for  $(100)$  plane the 'd' values increase systematically from  $4.74 \text{ \AA}^\circ$  (our ferberite) to  $4.76$  (natural

wolframite), 4.78 (synthetic wolframite) and 4.84 (hübnerite).

7. Our seven synthetic samples were chemically analysed and it was found that chemical analysis data were not fully reliable. SEM analysis (Table 3-11) however showed systematic variations in the Fe/Mn and Fe/W ratios. Atomic proportion of iron related to those of manganese and tungsten are somewhat higher than the theoretical values suggesting probable formation of iron oxide phases such as hematite. Mellor [7] has mentioned that 'ferberite may occur coated with hydrated iron oxide, or be so intergrown with it that both the outside, and the parts exposed by fracture or cleavage may be brown; some specimens are iridescent owing to thin film of oxide.'

In any case, our samples were fully characterised in terms of solid state composition. It may be emphasized that very few 'wolframite' samples - whether natural or synthetic - used by the previous workers have been characterised in such detail and in terms of quantitative elemental and phase composition.

8. During the dissolution of the synthetic wolframites with 1N NaOH, special attention was paid to the examination of the solid residues. X-ray diffraction studies revealed the existence of some new phases such as sodium tungstate in most cases and  $WO_3$  in a few cases. Occasionally ferberite

peaks were prominent indicating that iron was somewhat slow to be dissolved.

The SEM examination indicated that the residues were heterogenous in elemental composition. In most cases and particularly in ferberite samples the Fe/W ratio on the residue went up periodically, more than the original value, indicating preferential dissolution (in one case Fe/W atomic ratio was as high as 34.7). Compared to NaOH dissolution, NaCl dissolution caused less tungsten recovery but also less selective dissolution i.e. Fe/W ratio of the solid remained more or less steady. Whereas in the former case alkali might have resulted in insoluble coating of iron oxo-hydroxide, chloride ion dissolved iron in the latter case.

Manganese analysis on the solid residue showed that the process was less selective and Mn and W were dissolved almost with equal ease. Analysis of the solutions confirmed this trend even further. Ferberite-NaOH solution reaction for 30 minutes resulted in 28.6 p.c. recovery of W but only 1.12 p.c. recovery of iron; under identical condition 50.15% recovery of W was possible from hübnerite. Thus, manganese replacing iron in the wolframite structure seems to result in less compact lattice and faster and less selective dissolution.

## CONCLUDING REMARKS

Osseo-Asare showed [11] that thermodynamics disfavors alkali dissolution of stable scheelite or  $\text{CaWO}_4$  at high pH but favors action on Fe and Mn tungstates. Burkin reported [12,13] that oxygen promotes dissolution of wolframite in alkali. However, increasing partial pressure of oxygen results in an oxide coating, inhibiting further dissolution. Burkin proposed that the initial removal of tungsten may represent topotactic reaction. X-ray micro-analysis of polished sections of leached wolframite showed heavy coatings containing iron and manganese in the same ratio as in the parent wolframite, and little or no tungsten. X-ray diffraction showed no lines other than those of wolframite.

Burkin did not provide quantitative SEM data. Our experiments have yielded many more details and shown the quantitative aspects of a complicated phenomena.

Shamsuddin and Sohn [8] have thrown light on commercial alkali leaching of wolframite. Just as scheelite is coated with  $\text{CaCO}_3$  during digestion with  $\text{Na}_2\text{CO}_3$  solution [14], and the reduced kinetics of dissolution can be improved by complexing  $\text{Ca}^{++}$  with EDTA [15], similarly the inhibiting influence of iron can be countered by EDTA type complexing agents and wolframite dissolution in alkali can be hastened [12]. It is possible to work out an integrated flowsheet for dissolution of tungsten-bearing ores using alkali [9].



13. Burkin A.R., The Chemistry of Hydrometallurgical Processes, E and F.N. Spon Ltd., London, 1966, Pages 87-92.
14. Queneau P, and Cooke, S.R.B., The Kinetics of dissolution of Scheelite in alkaline aqueous solution, Trans. Met. Soc. of AIME, 245, 19689, Pages 2451-2459.
15. Konishi Y, Katada H. and Asai S, Kinetics of Dissolution of Scheelite in Aqueous  $\text{Na}_4\text{EDTA}$  Solutions, Metallurgical Transactions B, AIME, Vol. 183, June 1987, Pages 331-337.

# APPENDIX

## A) DISTINCTION BETWEEN STANDARD 'd' VALUES OF SYNTHETIC AND NATURAL WORLFRAMITE

TABLE - 1

Synthetic $\text{FeMn}(\text{WO}_4)_2$		Natural $(\text{Fe}, \text{Mn})\text{WO}_4$	
'd'	I	'd'	I
5.73	15	5.68	10
4.78	60	4.76	50
3.761	55	3.740	50
3.673	55	3.648	50
2.968	100	2.953	100
2.946	90	-	-
2.864	30	2.848	20
2.488	45	2.483	60
2.460	10	-	-
2.392	25	2.385	20
2.217	15	2.218	10
2.202	25	2.192	30
2.070	5	2.061	10
2.054	5	-	-
2.023	10	-	-
2.010	10	2.006	10
1.911	10	1.907	5
1.881	15	1.877	20
1.836	15	1.833	20
1.775	25	1.771	40
1.733	15	1.732	20
1.729	20		
1.719	25		
1.716	20	1.716	50
1.659	5	1.595	10

Table-1 contd...

Synthetic $\text{FeMn}(\text{WO}_4)_2$		Natural $(\text{Fe},\text{Mn})\text{WO}_4$	
'd'	I	'd'	I
1.594	10	1.514	20
		1.486	5
		1.467	20
		1.440	30
		1.391	5
		1.375	20
		1.321	10
		1.225	10
		1.194	20
		1.102	5
		1.086	5
		1.043	5

FIVE HIGHEST INTENSITY PEAKS FOR SYNTHETIC AND NATURAL WOLFRAMITE

TABLE - 2

Synthetic Wolframite			Natural Wolframite		
'd'	I	hkl	'd'	I	hkl
2.97	100	$11\bar{1}$	2.95	100	$\bar{1}11$
2.95	90	111	2.48	60	002
4.78	60	100	4.76	50	100
3.761	55	011	2.192	30	121,102
2.488	45	002,021	5.68	10	010

B) STANDARD 'd' VALUES FOR SYNTHETIC  $\text{MnWO}_4$

TABLE - 3

'd'	I	'd'	I
5.76	20	1.921	6
4.84	65	1.887	16
3.78	60	1.851	16
3.70	55	1.784	25
2.996	100	1.7666	6
2.954	95	1.7539	20
2.880	30	1.7440	20
2.497	55	1.7266	30
2.474	10	1.7196	20
2.416	20	1.6839	4
2.237	16	1.6777	6
2.209	25	1.6762	6
2.087	8	1.6472	4
2.057	12	1.5996	6
2.051	12	1.5501	2
2.021	10	1.5272	16

FIVE HIGHEST INTENSITY PEAKS FOR  $\text{MnWO}_4$

TABLE - 4

d	I	hkl
3.00	100	$\bar{1}11$
2.95	95	111
4.84	65	100
3.78	60	011
3.70	55	110

C) STANDARD 'd' VALUES FOR SYNTHETIC  $\text{FeWO}_4$ .

TABLE - 5

'd'	I	'd'	I
5.71	15	2.367	15
4.736	40	2.194	20
3.745	35	2.051	5
3.644	35	2.00	10
2.940	100	1.902	5
2.856	25	1.873	10
2.481	25	1.823	10
2.474	30	1.765	20
2.443	10	1.712	30

FIVE HIGHEST INTENSITY PEAKS FOR  $\text{FeWO}_4$

TABLE - 6

d	I	hkl
2.94	100	$\bar{1}11, 1\bar{1}\bar{1}$
4.74	40	100
3.75	35	011
2.474	30	021
5.71	15	010

D) STANDARD FIVE HIGHEST INTENSITY 'd' VALUES FOR

i) Fe : Mn  
80 : 20

TABLE - 7

d	I
2.695	72
1.485	64
4.871	100 +
3.686	67
2.949	64

ii) Fe : Mn  
60 : 40

TABLE - 8

d	I
2.404	94
3.686	86
4.836	81
2.949	65
1.485	62

iii) Fe : Mn  
40 : 60

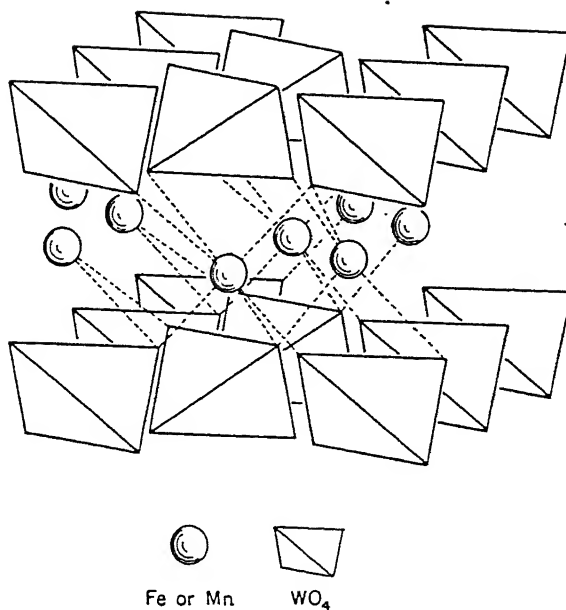
TABLE - 7

d	I
4.819	98
2.943	75
2.986	61.5
3.686	43
2.412	36

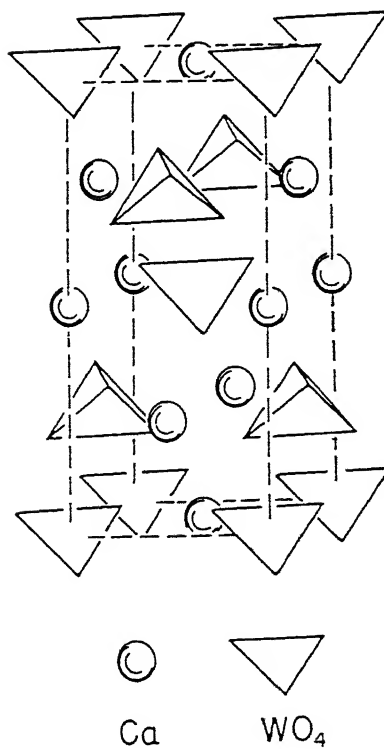
iv) Fe : Mn  
20 : 80

TABLE - 8

d	I
2.943	97
4.819	84
2.993	78
3.696	54
2.943	44



Wolframite structure



Scheelite structure.



## TUNGSTEN

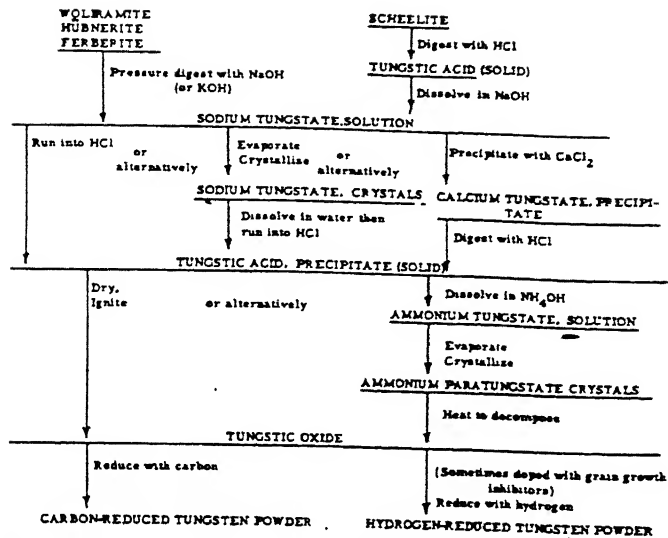


Figure 30.3. Composite of current industrial procedures for the processing of tungsten concentrates into metal powder.